

**ELECTRON TRANSFER REACTIONS. REACTION OF
SEVERAL OXYGEN AND NITROGEN HETEROCYCLES
WITH POTASSIUM**

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by
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to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
JANUARY, 1987

**Dedicated
To
My Parents**

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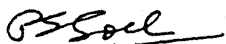
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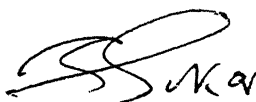
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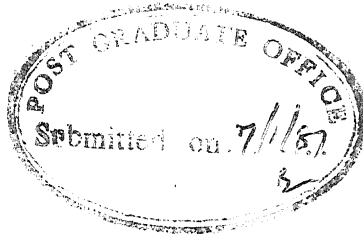
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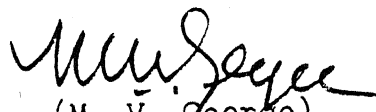
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CERTIFICATE II

Certified that the work embodied in this thesis entitled: 'ELECTRON TRANSFER REACTIONS. REACTION OF SEVERAL OXYGEN AND NITROGEN HETEROCYCLES WITH POTASSIUM' has been carried out by Mr. Mohammed Muneer under my supervision and the same has not been submitted elsewhere for a degree.


(M. V. George)
Thesis Supervisor

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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KANPUR,

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MOHAMMED MUNEER

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PREFACE

The thesis entitled: 'Electron Transfer Reactions. Reaction of Several Oxygen and Nitrogen Heterocycles with Potassium' is divided into four chapters.

Chapter I of the thesis deals with the reaction of oxazolones (1a-c, 12), bioxazolinediones (17, 26), furanones (30a-c), and bifurandiones (51, 63) with potassium in tetrahydrofuran (THF) under different conditions and with potassium superoxide in benzene containing 18-crown-6. These substrates gave a variety of products, depending upon the reaction conditions. The reaction of 1a with potassium, for example, gave a mixture of dibenzamide (11a, 12%), N-benzoyl-C-phenylglycine (6a, 27%) and C-phenylglycine (10a, 33%). A higher yield of 11a (40-55%) was obtained, together with 9 (30%) and 6a (7%), when the reaction of 1a was carried out either with potassium in THF, saturated with oxygen, or with potassium superoxide. Similar mixtures of products were obtained in the reactions of 1b, 1c and 12 with potassium. The reaction of the bioxazolinedione 17 with potassium gave a mixture of 11a (17%), 6a (8%), and 10a (14%), along with an appreciable yield of tetraphenylpyrazine (25, 41%), whereas the bioxazolinedione 26, under analogous conditions, gave

a mixture of 6b (15%), 15 (20%) and 29 (11%). Earlier studies from this laboratory had shown that several 2(3H)-furanones and bifurandiones react with potassium in THF to give a variety of products, arising through the formation of radical anion intermediates and their subsequent reaction with oxygen. The furanone 30a, for example, is reported to give a mixture of 1,3,3-triphenylprop-2-ene-1-one (40a, 7%) and benzoic acid (9, 60%). In order to understand the mechanistic details of the formation of these oxygenated products, the reactions of several furanones (30a-c, 60) and bifurandiones (51, 63) were reinvestigated under different conditions. The reaction of 30a with potassium in THF, saturated with oxygen, gave a mixture of β -benzoyl- α,α -diphenylpropanoic acid (36a, 12%), 1,3,3-triphenylprop-2-ene-1-one (40a, 14%), and benzoic acid (9, 57%), along with some recovered starting material (30a, 14%). Likewise, the reaction of 30b with potassium in THF gave a mixture of 36b (29%) and 40b (9%). Similarly, 30c, under analogous conditions, gave 39c (15%), 40c (10%), and 9 (41%). In contrast, the reaction of 60 with potassium in oxygen-saturated THF did not give any isolable product; only the starting material (60, 57%) could be recovered unchanged. Treatment of the bifurandione 63 with potassium in THF gave 3-phenyl-2(3H)-benzofuranone (60, 58%), as the only product.

Chapter II of the thesis deals with the reaction of several sydnones (1a-f) with potassium in THF. The reaction of 1a-f with

potassium gave a mixture of products consisting of the azo compounds 17a-c (1-2%), the bisazoalkenes 16a,b (2%), the phenylglyoxylic acid arylhydrazones 4a,b (31%), the amides 15a-c,e (14-20%), the amines 13a-c (11-26%), the nitroso compounds 5d-f (7-24%), and benzoic acid (14a, 3-11%). Similar mixtures of products were obtained when the reactions of 1a-f were carried out either with potassium in THF, saturated with oxygen or with potassium superoxide.

Chapter III of the thesis deals with the reaction of some nitrogen heterocycles such as indoles (1a-c), pyrroles (10a-c), oxazoles (45a-c) and 2,4,5-triphenylimidazole (50) with potassium in THF. Treatment of 1a with potassium in THF, for example, gave the carbazole 8a (49%), whereas 1c, under analogous conditions, gave a mixture of the carbazole 8c (20%) and the indole 1a (19%). The reaction of 1b with potassium gave 1a (68%), as the only isolable product. In contrast, the reaction of 1a,c with potassium in THF, saturated with oxygen gave a mixture of 2-benzamidobenzophenone (9a, 20-34%) and 2,3-diphenylindole (1a, 7-9%). An attempted reaction of a pyrrole such as 10a with potassium in THF did not yield any product; most of the starting material could be recovered unchanged. However, when the reaction of 10a was carried out with either potassium in THF, saturated with oxygen or with potassium superoxide, a

mixture of the lactam 17a (11-19%), the benzoylaminostilbene 22a (7-23%), tetraphenylpyrazine (33, 13-15%), benzamide (24a, 8-15%), and benzoic acid (23, 10-13%) was obtained. The reaction of N-substituted pyrroles 10b,c with potassium gave the N-unsubstituted pyrrole 13b (30-33%), whereas the reaction of 10b,c with potassium in THF, saturated with oxygen gave a mixture of 13b (7-8%), the lactam 17b (10-12%), the butanone 43b (12-14%), the 1,4-dione 44b (11-13%), the amides 24a-c (9-17%), and benzoic acid (23, 14-15%). In contrast, the reaction of 10b,c with potassium superoxide did not give any isolable product; most of the starting material could be recovered unchanged. Treatment of the oxazoles 45a-c with potassium gave a mixture of N-(1,2-diphenylethyl)-benzamide (48a, 27%), the N-vinylamides 49b,c (30-33%), and benzoic (23, 4-5%), whereas the reaction of the imidazole 50, under analogous conditions, did not yield any isolable product. However, treatment of 50 with potassium in THF, saturated with oxygen, gave dibenzamide (21a, 5%), as the only product. Similar results were obtained when the reactions of 45a-c were carried out with potassium superoxide.

Chapter IV of the thesis deals with the reaction of several oxygen containing substrates such as tetracyclone (1), furans (6a-c) and 2,3-diphenylindenone (31) with potassium and potassium

superoxide. An earlier report from this laboratory had indicated that tetracyclone (1), on treatment with potassium in THF, gives a mixture of tetraphenylfuran (6a, 5%), cis-dibenzoylstilbene (7, 19%), and benzoic acid (17, 20%), whereas, 6a under analogous conditions gives a mixture of 2,3-diphenylindenone (31, 10%) and a few unidentified products. Similarly, it had been reported that the reaction of 31 with potassium in THF gives a mixture of the dibenzofluorenone 44 (18%) and the 2-hydroxyindanone 48 (35%). Neckers and Hauck (J. Org. Chem., 48, 4691 (1983)) have shown that the reaction of tetracyclone (1) with potassium superoxide gives a mixture of the 2-hydroxyfuranone 18, the pyranone 15, and benzoic acid (17). To delineate the mechanistic details of the reaction of tetracyclone (1) and related substrates with potassium in THF and with potassium superoxide, we have reinvestigated the reaction of these substrates under different conditions. The reaction of 1 with potassium in THF, saturated with oxygen, for example, gave a mixture of products consisting of the 2-hydroxyfuranone 18 (8%), 6a (12%), 7 (5%), and benzoic acid (17, 53%). The reaction of 1 with potassium superoxide in benzene containing 18-crown-6 gave a mixture of tetraphenylfuran (6a, 4%), tetraphenylpyran-2-one (15, 23%), the 2-hydroxyfuranone 18 (46%), and benzoic acid (17, 25%). The reaction of 2,5-diphenylfuran (6b) with potassium gave benzoic acid (17, 46%), as the only isolable product. On the other hand, the reaction of 2,3,5-triphenylfuran (6c) with potassium gave a mixture of several products, in each

case. Thus, in the reaction of 6c with potassium, a mixture of products consisting of the butanone 32c (21%), the 1,4-dione 38c (9%), the 2-hydroxy-1,4-dione 37c (7%), and benzoic acid (17, 14%) was obtained. Similarly, the reaction of 6a with potassium gave a mixture of the butanone 32a (25%), 2,3-diphenylindenone (31, 18%), 3-benzoyl-2-hydroxyindanone 26 (35%), and cis-dibenzoylstilbene (7, 5%). The reaction of 2,3-diphenylindenone (31) with potassium has been investigated and found to give a mixture of products consisting of the dibenzofluorenone 44 (33%), 2-hydroxy-2,3-diphenylindanone (48, 30%), 2,3-diphenylbenzofuran (47, 2%), and benzoic acid (17, 5%).

Reasonable mechanisms have been suggested to account for the formation of the various products in the reaction of different substrates listed under Chapters I-IV. Cyclic voltammetric studies have been carried out using these substrates to measure the reduction potentials for both one electron and two electron processes leading to the corresponding radical anion and dianion intermediates. The radical anions of these substrates have also been generated through pulse radiolysis in methanol and their absorption spectra were recorded.

Note : The numbers of the various compounds given in parentheses correspond to those given under the respective chapters.

CHAPTER I

ELECTRON TRANSFER REACTIONS. REACTION OF OXAZOLINONES, BIOXAZOLINEDIONES, FURANONES, AND BIFURANDIONES WITH POTASSIUM

I.1 ABSTRACT

The reaction of several Δ^2 -oxazolin-5-ones (1a-c, 12), bioxazolinediones (17, 26), furanones (30a-c, 53, 60), and bifurandiones (51, 63) with potassium in tetrahydrofuran (THF) has been examined. Some of the oxazolinones that we have studied include 2,4-diphenyl- Δ^2 -oxazolin-5-one (1a), 4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one (1b), 2,4,4-triphenyl- Δ^2 -oxazolin-5-one (1c), and 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (12). The reaction of 1a with potassium in THF gave a mixture of dibenzamide (11a, 12%), N-benzoyl-C-phenylglycine (6a, 27%), and C-phenylglycine (10a, 33%). A higher yield of 11a (40%) was obtained together with benzoic acid (9, 30%), when the reaction of 1a was carried out in THF, saturated with oxygen. Under analogous conditions, 1b gave a mixture of β -phenylalanine (10b, 37%) and benzoic acid (9, 33%), along with some unchanged starting material (1b, 6%). The reaction of 1c, however, gave a mixture of N-benzoyl-C,C-diphenylglycine (6c, 30%) and N-benzoyl-C,C-diphenylmethanamine (5c, 57%). Similarly, the reaction of 12 gave a mixture of N-benzoylaminocinnamic acid (15, 39%) and benzoic acid (9, 39%). The reaction of

bioxazolidinediones such as bi-4,4'-(2,4-diphenyl- Δ^2 -oxazolin-5-one) (17) and bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (26) with potassium in THF has also been investigated. The reaction of 17 with potassium, for example, gave a mixture of 11a (17%), 6a (8%), 10a (14%), and tetraphenylpyrazine (25, 41%), whereas the bioxazolidinedione 26, under analogous conditions, gave a mixture of 15 (20%), N-benzoyl- β -phenylalanine (6b, 15%) and benzamide (29, 11%).

In continuation, we have examined the reaction of furanones and bifurandiones with potassium in THF, saturated with oxygen and also with potassium superoxide in benzene. The furanones that we have studied include 3,3,5-triphenyl-2(3H)-furanone (30a), 3-methyl-3,4,5-triphenyl-2(3H)-furanone (30b), 3,3,4,5-tetraphenyl-2(3H)-furanone (30c), 3,4,5-triphenyl-2(5H)-furanone (53), and 3-phenyl-2(3H)-benzofuranone (60). In addition, the reaction of a bifurandione such as 3,3'-diphenyl-3,3'-bibenzofuran-2,2' (3H,3'H)-dione (63) with potassium has also been studied. The reaction of 30a with potassium in THF, saturated with oxygen gave a mixture of β -benzoyl- α,α -diphenylpropanoic acid (36a, 12%), 1,3,3-triphenylprop-2-ene-1-one (40a, 14%), and benzoic acid (9, 57%), along with some recovered starting material (30a, 14%). The reaction of 40a itself, under analogous conditions, gave a mixture of benzophenone (46, 8%), 1,3,3-triphenylprop-1-one (45, 49%), and benzoic acid (9, 10%). Likewise, the reaction of

30b with potassium in THF gave a mixture of β -benzoyl- α,β -diphenyl- α -methylpropanoic acid (36b, 29%) and 1,2,3-triphenylbut-2-ene-1-one (40b, 9%). Similarly, the reaction of 30c with potassium in THF, saturated with oxygen gave a mixture of 3,3,4,5-tetraphenyl-5-hydroxyfuran-2-one (39c, 15%), 1,2,3,3-tetraphenylprop-2-ene-1-one (40c, 10%), and benzoic acid (9, 41%). The reaction of 3,4,5-triphenyl-2(5H)-furanone (53) with potassium in THF, saturated with oxygen gave 2,3-diphenylpropenoic acid (59, 70%), benzoic acid (9, 15%) and the unchanged starting material (53, 5%). In contrast, the reaction of 3-phenyl-2(3H)-benzofuranone (60) with potassium in oxygen-saturated THF did not give any isolable product; only the starting material (60, 57%) could be recovered unchanged. Treatment of the bifurandione (63) with potassium in THF gave 3-phenyl-2(3H)-benzofuranone (60, 58%) as the only isolable product.

Reasonable mechanisms, involving the initial formation of radical anion intermediates and their subsequent transformation to give the observed products have been suggested. Cyclic voltammetric studies have been carried out to measure the reduction potentials of these substrates in the generation of their radical anions. The radical anions of these substrates were also generated pulse radiolytically in methanol and their spectra showed absorption maxima in the region 295-350 nm.

I.2 INTRODUCTION

Alkali metals react with unsaturated organic compounds

through electron transfer reactions to give radical anion and dianion intermediates, which in turn, undergo a variety of transformations, depending on the reaction conditions.¹ Earlier studies² had shown that several 2(3H)-furanones and bifurandiones react with potassium in THF to give a variety of products, arising through the formation of radical anion intermediates and their subsequent reaction with oxygen. The object of the present investigation has been to examine the reactions of some representative Δ^2 -oxazolin-5-ones and bioxazolin-5-ones with potassium in THF, to study the type of products formed in these cases and also their reaction pathways. Also, it was felt necessary to reinvestigate the reactions of several 2(3H)-furanones and bifurandiones with potassium in THF, to understand the role of oxygen in the formation of the oxygenated products in these reactions.

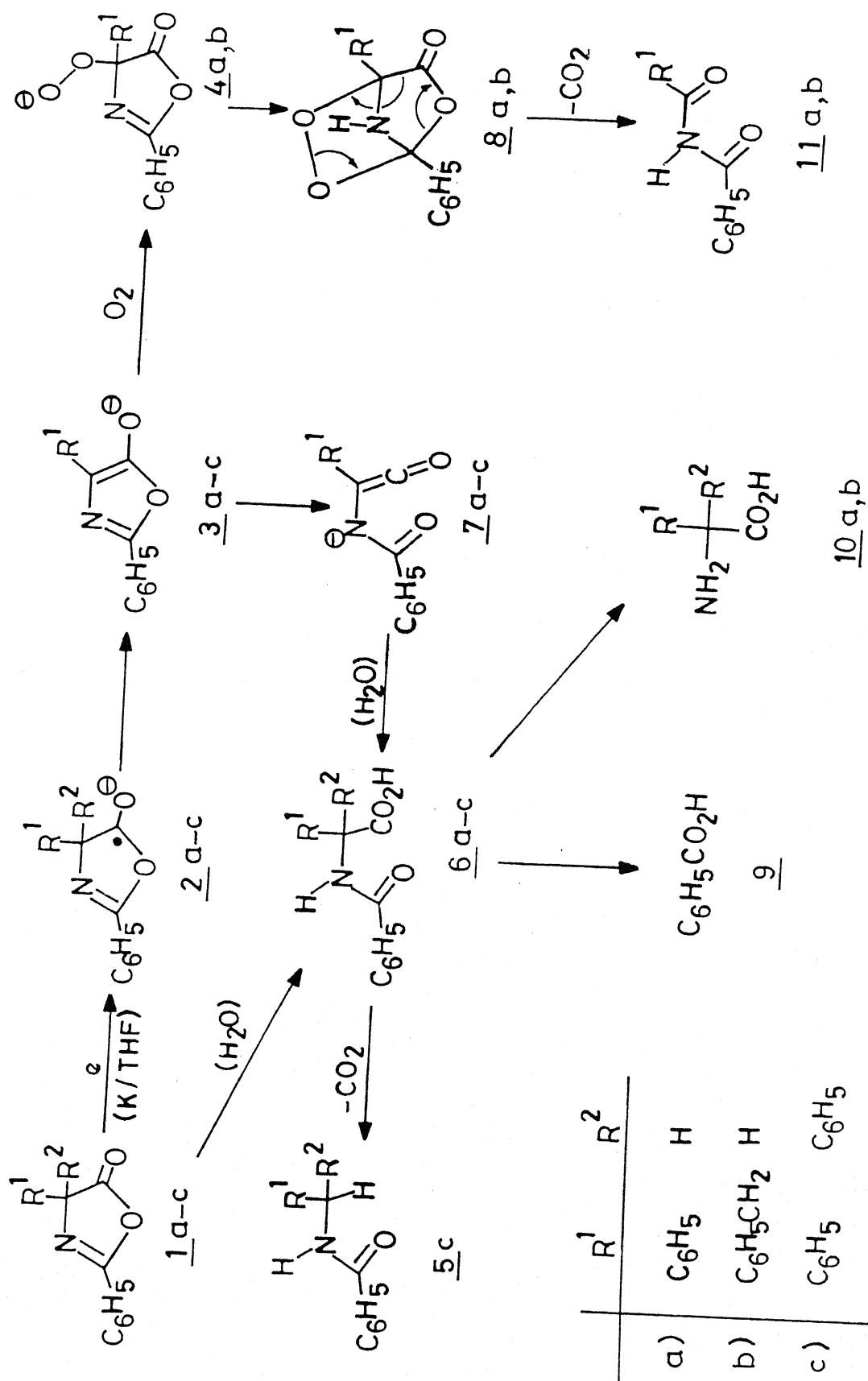
I.3 RESULTS AND DISCUSSION

In the present study, we have examined, the reaction of 2,4-diphenyl- Δ^2 -oxazolin-5-one (1a), 4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one (1b), 2,4,4-triphenyl- Δ^2 -oxazolin-5-one (1c), and 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (12). In addition, the reaction of two bioxazolin-5-ones such as bi-4,4'-(2,4-diphenyl- Δ^2 -oxazolin-5-one) (17) and bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (26) has been investigated.

The reaction of 1a with potassium in THF, for example, gave a mixture of dibenzamide (11a, 12%), N-benzoyl-C-phenylglycine (6a, 27%), and C-phenylglycine (10a, 33%). When the reaction of 1a with potassium, however, was carried out in THF, saturated with oxygen, a much higher yield of 11a (40%) was obtained, along with appreciable amounts of benzoic acid (9, 30%). The reaction of 1b with potassium in THF gave a mixture of β -phenylalanine (10b, 37%) and benzoic acid. Under analogous conditions, the reaction of 1c with potassium in THF gave a mixture of N-benzoyl-C, C-diphenylglycine (6c, 30%) and N-benzoyl-C,C-diphenylmethanamine (5c, 57%). On the other hand, when the reaction of 1c with potassium was carried out in oxygen-saturated THF, a mixture of 6c (15%), and benzoic acid (9, 25%) was formed.

The formation of the different products in the reaction of 1a-c with potassium in THF could be understood in terms of the pathway shown in Scheme I.1. It has been assumed that the initial step in the reaction involves an electron transfer process leading to the formation of the radical anions 2a-c, which can, through the loss of a hydrogen atom, give the anionic intermediates 3a,b. These intermediates (3a,b), in turn, can lead to the carboxylic acids 6a,b, through the corresponding ketene intermediates 7a,b. The carboxylic acids 6a-c can also be directly formed from 1a-c, under the hydrolytic conditions of workup. Products such as 5c, 9 and 10a,b in these reactions,

Scheme I.1



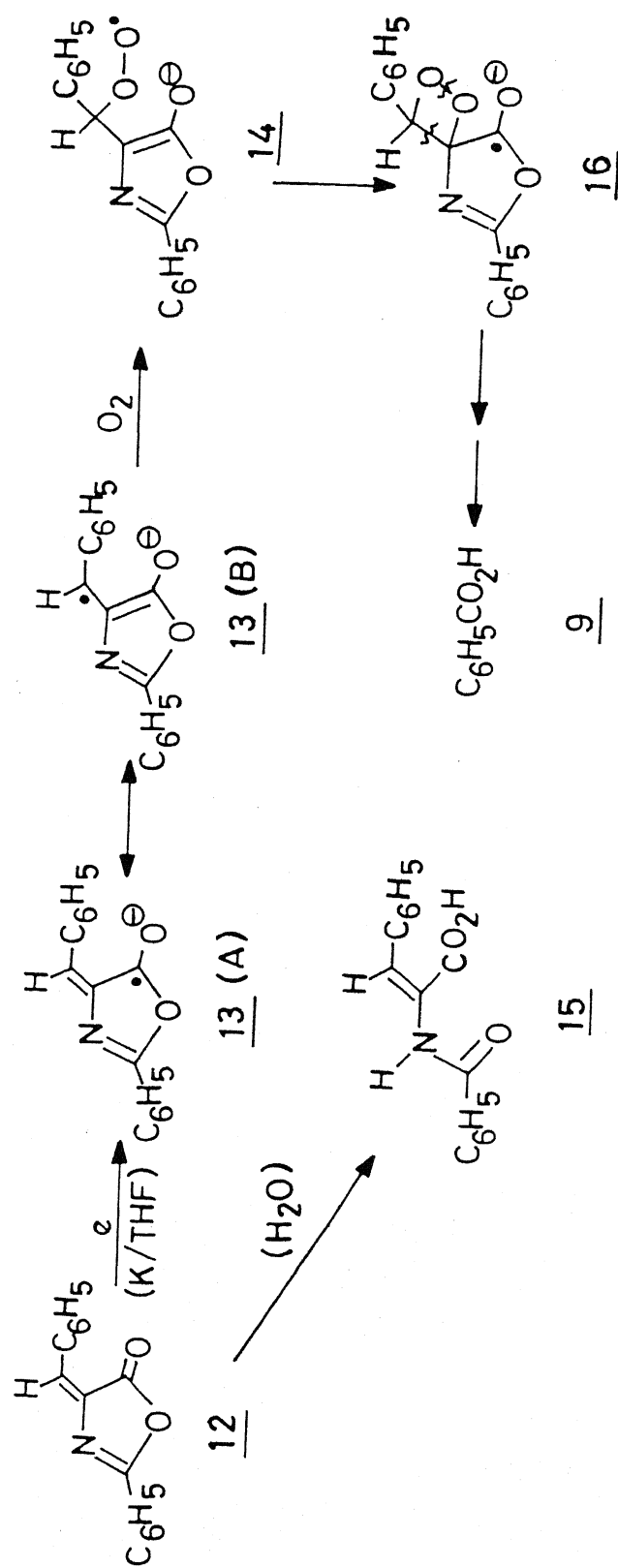
however, could arise through the further transformations of 6a-c. The formation of 11a,b, on the other hand could be understood in terms of the reaction of 3a,b with oxygen, under workup conditions to give the hydroperoxy intermediates 4a,b which will then lead to the observed products through the endoperoxides 8a,b. The fact that enhanced yields of 11a were obtained in the reaction of 1a with potassium in THF, saturated with oxygen and also when treated with potassium superoxide in benzene containing 18-crown-6, would support the involvement of oxygen and superoxide in the transformations of 1a-c, as implicated in Scheme I.1. The reaction of 1b with potassium superoxide in benzene likewise, gave a mixture of oxygenated products, N-benzoylphenylacetamide (11b, 21%), N-benzoyl- β -phenylalanine (6b, 23%), and benzoic acid (9, 46%), whereas the reaction of 1c with potassium superoxide, under analogous conditions, gave an excellent yield of N-benzoyl-C,C-diphenylglycine (6c, 85%). It may be mentioned in this connection that the recent studies by Chuaqui et al.³ have shown that the reaction of potassium superoxide with Δ^2 -oxazolin-5-one gives different products depending on the substituents present in the oxazolinone ring system. Thus, the reaction of 4,4-dimethyl-2-phenyl- Δ^2 -oxazolin-5-one with potassium superoxide gave a ring opened product, N-benzoyl- α -amino-isobutyric acid, whereas the reaction of 4-ethyl-2-phenyl- Δ^2 -oxazolin-5-one gave a mixture of N-benzoyl- α -aminobutyric acid

and N-benzoylpropionamide. The formation of the ring opened α -amino acid derivatives in these reactions has been explained in terms of the initial nucleophilic attack of the superoxide on the starting Δ^2 -oxazolin-5-one, followed by further transformations. The formation of N-benzoylpropionamide in the reaction of 4-ethyl-2-phenyl- Δ^2 -oxazolin-5-one, however, has been explained in terms of a 1,3-dipolar cycloaddition of singlet oxygen to the N-protonated zwitterionic form of the oxazolinone, followed by the loss of CO_2 and further transformations. We feel that under our reaction conditions, the pathway shown in Scheme I.1, involving the intermediates 2a-c may be operative.

The reaction of 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (12) with potassium in THF gave a mixture of N-benzoylaminocinnamic acid (15, 39%) and benzoic acid (9, 39%). The formation of these products, on the basis of analogy to the reactions of other Δ^2 -oxazolinones, can be rationalized in terms of the pathway shown in Scheme I.2.

The reaction of a bioxazolidinedione such as 17 with potassium in THF gave a mixture of dibenzamide (11a, 17%), N-benzoyl-C-phenylglycine (6a, 8%),⁴ C-phenylglycine (10a, 14%),⁴ and 2,3,5,6-tetraphenylpyrazine (25, 41%) (Scheme I.3), whereas, the reaction of 26 with potassium in THF gave a mixture of N-benzoylaminocinnamic acid (15, 20%),⁴ N-benzoyl- β -phenylalanine

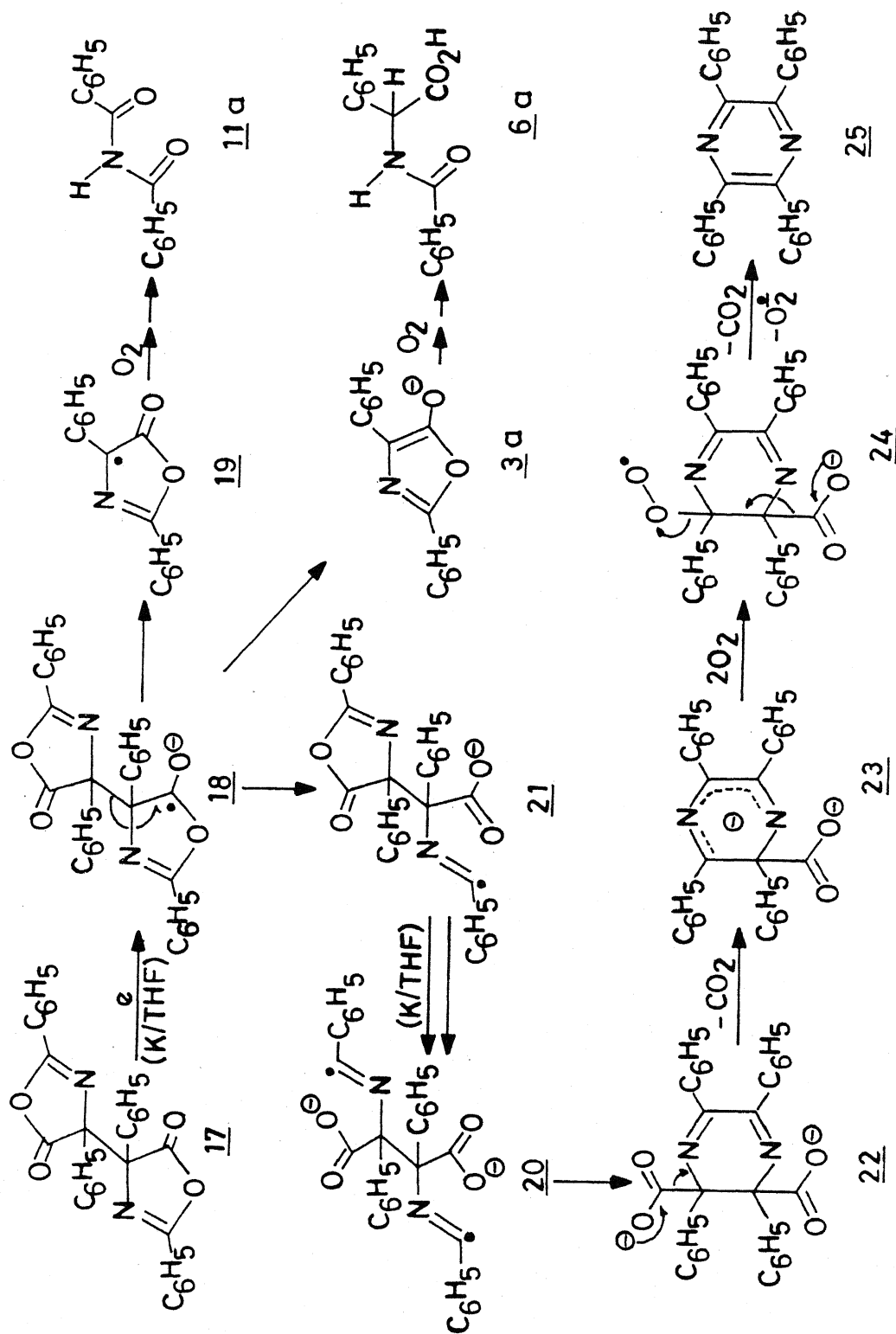
Scheme I.2



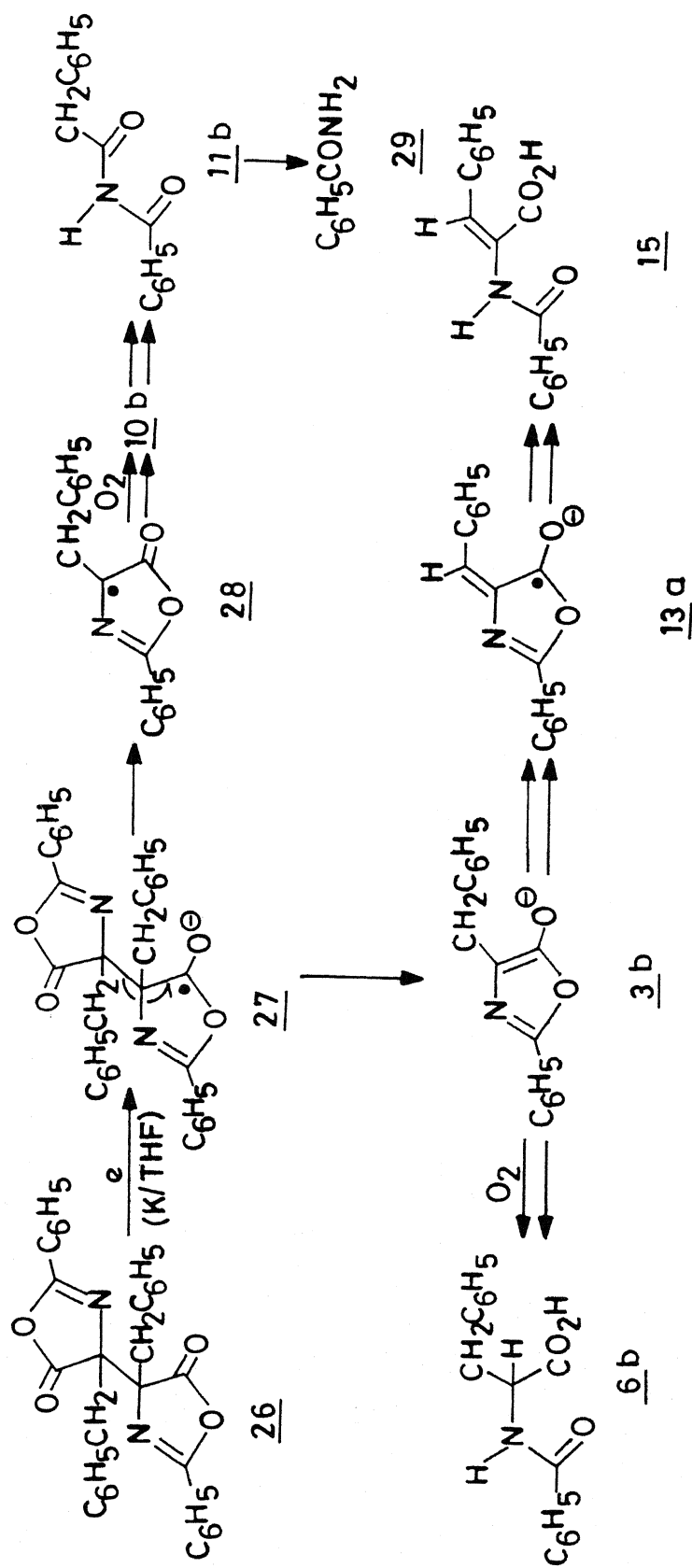
(6b, 15%), and benzamide (29, 11%)⁴ (Scheme I.4). The reaction of 26 with potassium superoxide, however, gave a mixture of 15 (28%)⁴ and benzoic acid (9, 21%).⁴ The formation of the different products in the reaction of 17 and 26 with potassium in THF could be rationalized in terms of the pathways shown in Schemes I.3 and I.4. The initially formed radical anion 18 in the case of 17, for example, could undergo fragmentation to give both the radical 19 and the anionic species 3a, which in turn can lead to 11a and 6a, respectively, as shown in Scheme I.3. The radical anion intermediate 18 can also undergo transformation to give 21, which could ultimately be converted to 2,3,5,6-tetraphenylpyrazine (25), through the intermediates 20, 22, 23 and 24, as shown in Scheme I.3. It may be pointed out here that 25 has been reported to be formed from 17 in small amounts under thermal conditions.⁵ Similarly, the radical anion 27 formed from 26 could lead to the different products as shown in Scheme I.4.

The reactions of several 2(3H)-furanones such as 3,3,5-triphenyl-2(3H)-furanone (30a), 3-methyl-3,4,5-triphenyl-2-(3H)-furanone (30b), 3,3,4,5-tetraphenyl-2(3H)-furanone (30c) and a bifurandione such as 2,2',3,3',4,4'-hexaphenyl-2,2'-bifuran-5,5'(2H,2'H)-dione (51) with potassium in THF have been reported earlier.² The reaction of 3,3,5-triphenyl-2(3H)-furanone (30a) with potassium in THF, for example, gave a

Scheme I.3



Scheme I.4



mixture of β -benzoyl- α,α -diphenylpropanoic acid (36a, 17%), 1,3,3-triphenylprop-2-ene-1-one (40a, 14%), and benzoic acid (9, 39%), besides a 22% recovery of the unchanged starting material (30a) (Scheme I.5). The formation of the oxygenated products in these reactions has been alluded to the reaction of adventitious oxygen with the initially formed radical anion intermediates. In order to understand the mechanistic details of these reactions, we have reinvestigated the reaction of several 2(3H)-furanones and bifurandiones with potassium in THF, under different conditions.

In this connection, we have examined the reactions of 3,3,5-triphenyl-2(3H)-furanone (30a), 3-methyl-3,4,5-triphenyl-2(3H)-furanone (30b), 3,3,4,5-tetraphenyl-2(3H)-furanone (30c), 3,4,5-triphenyl-2(5H)-furanone (53), 3-phenyl-2(3H)-benzofuranone (60), 2,2',3,3',4,4'-hexaphenyl-2,2'-bifuran-5,5' (2H,2'H)-dione (51), and 3,3'-diphenyl-3,3'-bibenzofuran-2,2' (3H,3'H)-dione (63).

The reaction of 30a with potassium in THF for 20 h, for example, gave a mixture of β -benzoyl- α,α -diphenylpropanoic acid (36a, 11%), 1,3,3-triphenylprop-2-ene-1-one (40a, 13%), benzoic acid (9, 57%),^{6a} and a small amount (14%) of the unchanged starting material (30a). Similar product mixtures consisting of 36a, 40a, and 9 were obtained when the reaction

of 30a was carried out with excess of potassium and also when the reaction mixture was saturated with oxygen before workup. Similarly, when the reaction of 30b was carried out with potassium in THF and the mixture was saturated with oxygen before workup, a mixture of products consisting of β -benzoyl- α,β -diphenyl- α -methypropanoic acid (36b, 28%), 1,2,3-triphenylbut-2-ene-1-one (40b, 9%), and benzoic acid (9, 5%)^{6a} was obtained. In addition, a small amount (9%) of the unchanged starting material (30b) could also be recovered from this reaction. Likewise, the reaction of 30c with potassium in THF, followed by saturation with oxygen before workup gave a mixture of 3,3,4,5-tetraphenyl-5-hydroxyfuran-2-one (39c, 15%), 1,2,3,3-tetraphenylprop-2-ene-1-one (40c, 10%), benzoic acid (9, 41%),^{6a} and the unchanged starting material (30c, 21%).

The formation of the different products in the reaction of 30a-c with potassium in THF under degassed conditions and in the presence of oxygen could be understood in terms of the pathway shown in Scheme I.5. It has been assumed that the initial step in the reaction of 2(3H)-furanones 30a-c with potassium is an electron transfer process, leading to radical anion intermediates 31a-c, which can then react with oxygen to give back the starting furanone and potassium superoxide. Mention may be made in this connection that several examples of superoxide formation by electron transfer to oxygen from

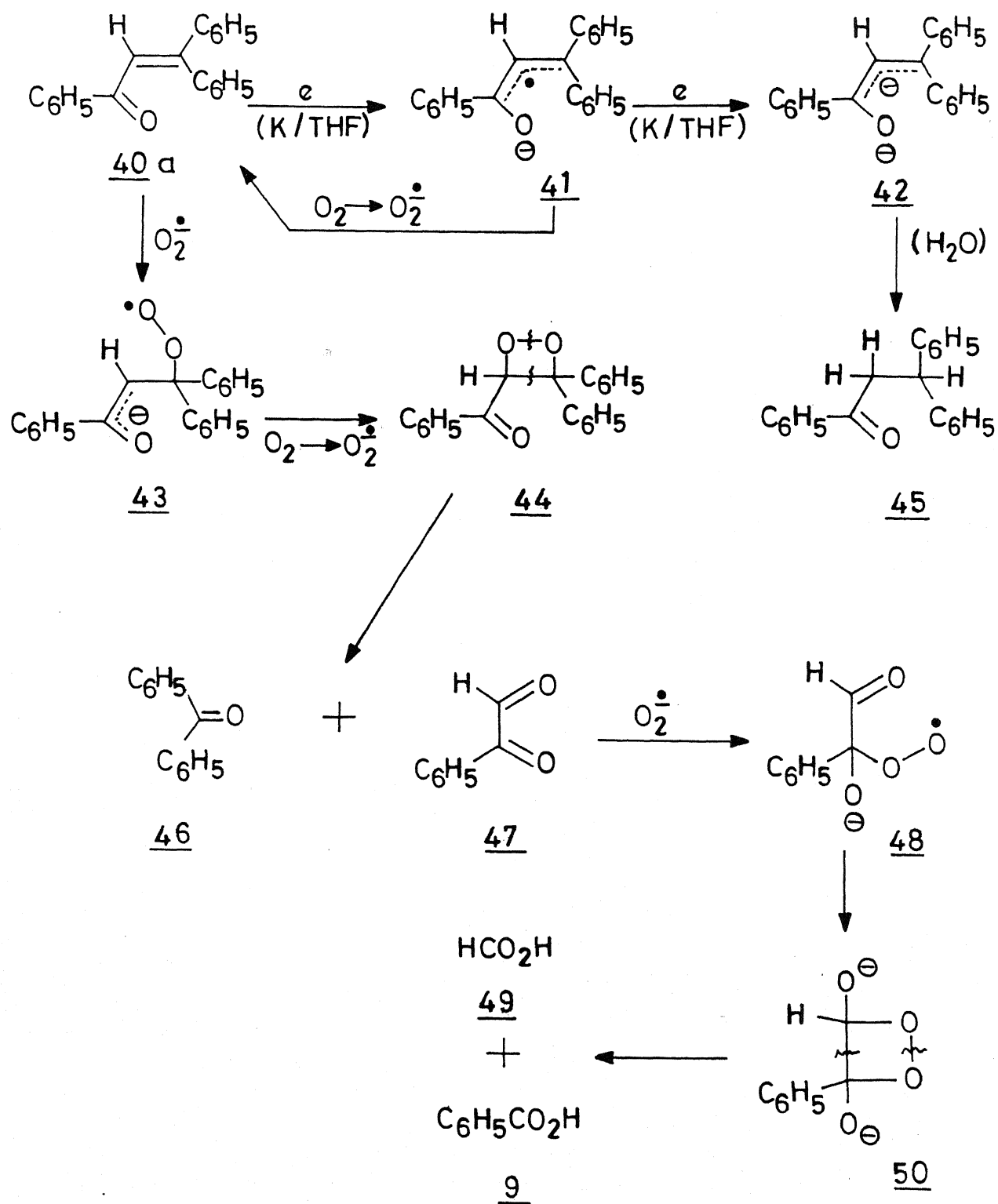
radical anions and also by electrochemical method are reported in the literature.⁷ Subsequent reactions of superoxide with 30a-c could ultimately lead to the different products, as shown in Scheme I.5.

Support for the involvement of superoxide in the transformation of furanones 30a, 30b, and 30c has been derived from the isolation of the same product mixtures in the reaction of these furanones with potassium superoxide. Thus, the treatment of 30a with potassium superoxide in benzene containing 18-crown-6 gave a mixture of β -benzoyl- α,α -diphenylpropanoic acid (36a, 52%), 1,3,3-triphenylprop-2-ene-1-one (40a, 9%), benzoic acid (9, 19%),^{6a} and a small amount (13%) of the unchanged starting material (30a). Similarly, when 3,3,4,5-tetraphenyl-2(3H)-furanone (30c) was treated with potassium superoxide, under analogous conditions, a mixture of 3,3,4,5-tetraphenyl-5-hydroxyfuran-2-one (39c, 50%), 1,2,3,3-tetraphenylprop-2-ene-1-one (40c, 7%), benzoic acid (9, 25%),^{6a} and some unchanged starting material (30c, 13%) was obtained.

To examine whether the α,β -unsaturated ketones 40a-c formed in the reaction of furanones 30a-c with potassium in THF and potassium superoxide, undergo further transformations, leading to benzoic acid and other products, we have carried out separately the reaction of 1,3,3-triphenylprop-2-ene-1-one (40a) with potassium in THF. Treatment of 40a with excess

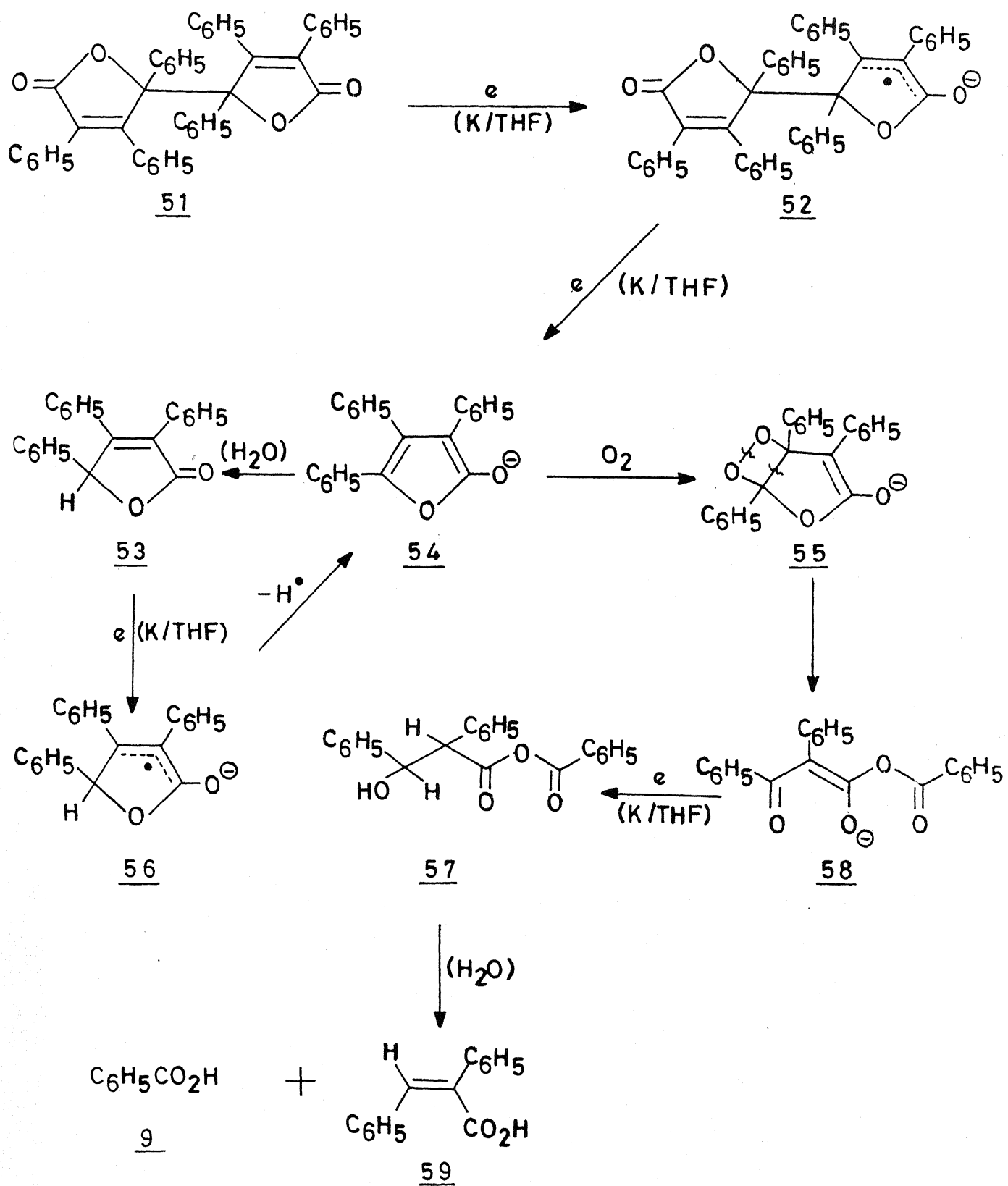
potassium in THF, followed by saturation of the reaction mixture with oxygen before workup gave a mixture of benzophenone (46, 8%), β,β -diphenylpropiophenone (45, 49%), benzoic acid (9, 10%),^{6a} and unchanged starting material (40a, 28%). The formation of the different products in the reaction of 40a could be understood in terms of the pathway shown in Scheme I.6, involving radical anion (41) and dianion (42) intermediates. The radical anion intermediate 41, for example, can react with oxygen to give superoxide, which in turn, interacts with the starting material (40a) to give ultimately benzoic acid (9) and benzophenone (46). The dianion intermediate 42, on the other-hand, can give rise to β,β -diphenylpropiophenone (45), on workup. In support of the assumption that products such as 46 and 9 arise through the superoxide reaction of 40a, we have shown, in a separate experiment, that the treatment of 40a with potassium superoxide in benzene containing 18-crown-6 gives a mixture of benzophenone (46, 38%), and benzoic acid (9, 25%),^{6a} along with some (30%) unchanged starting material (40a). It may be mentioned in this connection that Rosenthal and Frimer⁸ had observed earlier that potassium superoxide reacts with different α,β -unsaturated ketones in aprotic solvents to give a mixture of carboxylic acids.

The reaction of a bifurandione such as 2,2',3,3',4,4'-hexaphenyl-2,2'-bifuran-5,5' (2H,2'H)-dione (51) with excess of potassium in THF gave a mixture of 3,4,5-triphenyl-2(5H)-

Scheme I.6

furanone (53, 32%), 2,3-diphenylpropenoic acid (59, 29%), and benzoic acid (9, 22%).^{6b} A probable pathway for the formation of the different products from 51 is shown in Scheme I.7. It has been assumed that the radical anion intermediate 52, formed through electron transfer reaction, fragments to the anionic species 54, which on workup will give 53. Further reaction of 53 with potassium will lead ultimately to 59 and benzoic acid (9). In support of this assumption, it has been observed that the reaction of 53 with potassium in THF, in a separate experiment, leads to a mixture of 59 (70%) and benzoic acid (9, 18%), along with a small amount (8%) of the unchanged starting material (53). Further, it has been observed that the reaction mixture obtained on treatment of 53 with potassium under analogous conditions, in a separate experiment, when saturated with oxygen before workup gives a mixture of 59 (72%), and benzoic acid (9, 15%), along with a small amount (5%) of the starting material (53). The formation of 59 and 9 from 53 through oxidation with superoxide, as shown in Scheme I.7, was supported by the observation that potassium superoxide oxidation of 53 in benzene containing 18-crown-6 gave the same mixture of products, consisting of 59 (65%) and benzoic acid (9, 25%).

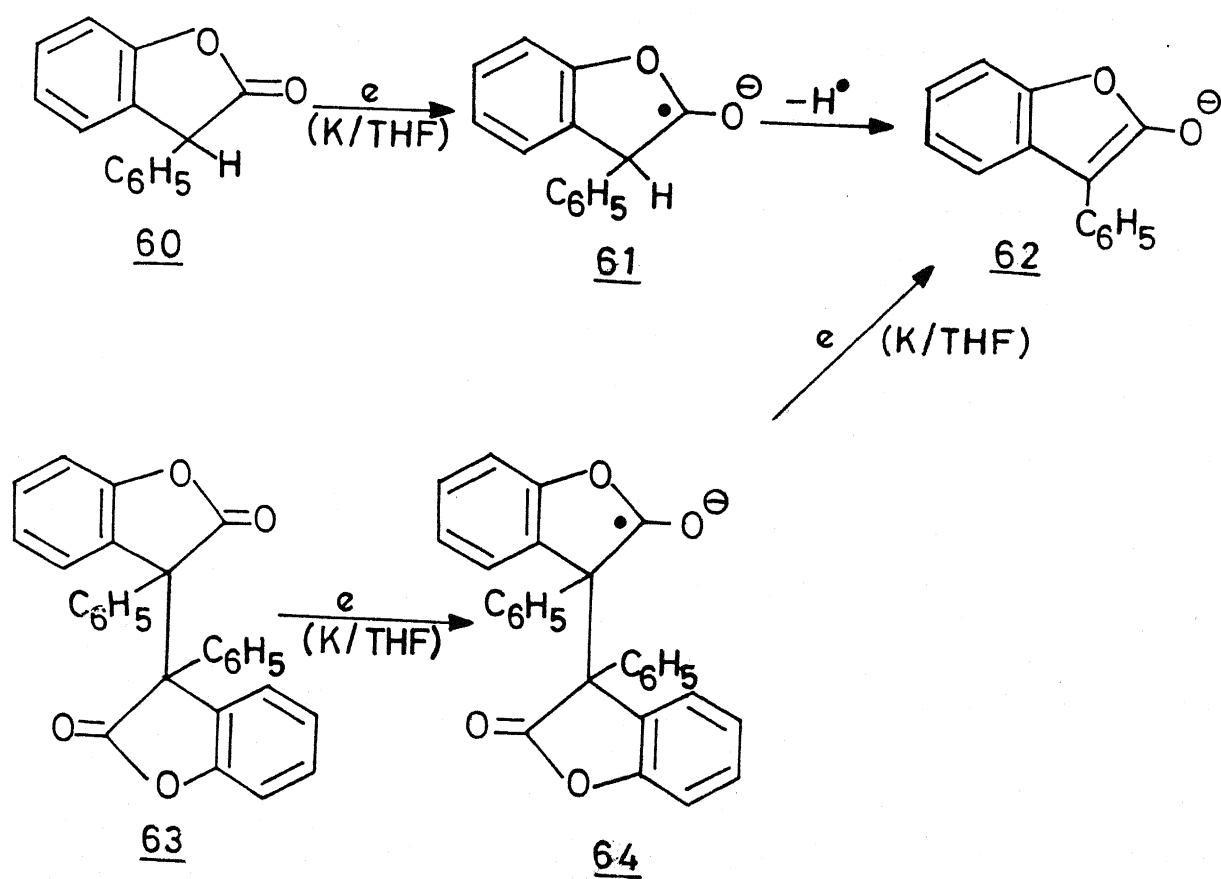
In contrast to the reactions of 30a-c and 53, the reaction of 3-phenyl-2(3H)-benzofuranone (60) with potassium in THF did not give any isolable product; only the starting material

Scheme 1.7

(60, 67%) could be recovered unchanged (Scheme I.8). Similarly, when the reaction mixture, obtained on treatment of 60 with potassium under analogous conditions, was saturated with oxygen before workup, again only the starting material (60, 57%) could be recovered. The apparent inertness of 60 could be understood in terms of the formation of the radical anion 61, which under the conditions of workup will give back the starting material (Scheme I.8). It is interesting to note that the reaction of the bibenzofurandione 63 with potassium in THF, however, gave a 58% yield of benzofuranone 60. It is likely that the radical anion 64, formed in this case may be fragmenting to the anionic species 62, which on workup will give 60 (Scheme I.8).

I.4 CYCLIC VOLTAMMETRIC STUDIES⁹

To examine whether radical anion intermediates such as 2a-c, 13, 18, 27, 31a-c, 41, 52, 56, and 61 are involved in the reaction of the different oxazolinones, bioxazolinodiones, furanones and bifurandiones under investigation, an attempt was made to generate these intermediates electrochemically and to characterize them through their reduction potentials and electronic spectra. The values of the reduction potentials of the Δ^2 -oxazolinones 1a-c and 12, bioxazolinodiones, 17 and 26, furanones 30a-c, 53 and 60 and bifurandiones 51 and 63,

Scheme 1.8

measured with respect to Ag/Ag^+ reference electrode are given in Tables I.1 and I.2. The cyclic voltammograms of the oxazolinones 1a-c and 12 and bioxazolinediones 17 and 26 are shown in Figure I.1, whereas, the cyclic voltammograms of some representative furanones and related substrates (30a, 40a, 51, 53, 60 and 63) are shown in Figure I.2. All the oxazolinones and bioxazolinediones under investigation exhibited irreversible reduction peaks with the reduction potentials in the range of -0.9 to -2.35 V versus Ag/Ag^+ reference. Similarly, compounds 30a, 51, 53 and 63 exhibited irreversible peaks while 40a exhibited both a reversible and an irreversible peak. The single reduction peak observed in the case of 30a-c, 51 and 60 were between -2.26 V and -2.70 V, which were attributed to the formation of the corresponding radical anions, 31a-c, 52 and 61, respectively (Schemes I.5, I.7 and I.8). In the case of the bifurandiones 51 and 63, however, two reduction peaks were observed corresponding to the radical anion 52 and 64, respectively (Schemes I.7 and I.8). Two reduction potentials were also observed for 40a at potentials -1.96 V and -2.4 V, respectively. These peaks have been attributed to the corresponding radical anion 41 and dianion 42, respectively (Scheme I.6).

To characterize the radical anions generated from the oxazolinones, bioxazolinediones, furanones and bifurandiones, we have electrochemically reduced these substrates in acetonitrile, in a specially designed cell, applying the

Table I.1 Electrochemical, spectral and kinetic data of oxazolinones and bioxazolinones

| Substrate | Reduction peak potential (E_p) ^a (V vs Ag/Ag ⁺) | Absorption maxima (nm) | | $k_{-b,c}$ $10^{10} M^{-1} s^{-1}$ | $\tau_{1/2}^{b,d}$ μs |
|-----------|---|--------------------------------|----------------------------|---------------------------------------|-------------------------------|
| | | Starting material ^a | Radical anion ^b | | |
| <u>1a</u> | -1.05 | 235 | 315 | 1.1 | 4.5 |
| <u>1b</u> | -1.10 | 240, 340, 360, 380 | 295 | 1.6 | 2.3 |
| <u>1c</u> | -2.35 | 247 | 295 | 1.6 | 2.3 |
| <u>12</u> | -1.56 | 258, 344, 360, 386 | 390 | 2.0 | 2.3 |
| <u>17</u> | -0.9, -1.33, -1.55 | 222 | 310 | 1.1 | 5.3 |
| <u>26</u> | -1.4, -1.58, -1.87 | 244 | 350 | 1.5 | 214.0 |

a) In acetonitrile containing 0.1 M tetrabutylammonium perchlorate. b) In methanol. c) Rate constant for the reaction of the substrate with solvated electron in methanol. d) Half-life of the radical anion in methanol.

Table I.2 Reduction potentials and spectral data of furanones, bifurandiones and α,β -unsaturated ketones

| Substrate | Reduction peak potential (E_p) ^a (V vs Ag/Ag ⁺) | Absorption maxima | | | | |
|------------|---|------------------------|--|------------------------|---|--|
| | | Starting materials | | Radical anions | | |
| | | λ_{\max} nm | ϵ_{\max} $10^3 \text{ l.mol}^{-1} \text{ cm}^{-1}$ | λ_{\max} nm | $\epsilon_{\max}^{\text{b,c}}$ $10^3 \text{ l.mol}^{-1} \text{ cm}^{-1}$ | |
| <u>30a</u> | -2.70 | 270 | 21.7 | 290,360 | 36.6,3.0 | |
| <u>30b</u> | -2.50 | 273 | 18.6 | 290,390 | 50.0,1.5 | |
| <u>30c</u> | -2.48 | 279 | 14.0 | 285,380 | 18.5,2.2 | |
| <u>40a</u> | -1.96,-2.40 | 300 | 12.5 | 345 | 8.35 | |
| <u>51</u> | -1.25,-1.95 | 283 | 24.7 | 425 | 1.60 | |
| <u>53</u> | -2.26 | 279 | 20.6 | 420 | 23.80 | |
| <u>60</u> | -2.65 | 269 | 2.1 | 345 | 16.00 | |
| <u>63</u> | -1.65,-2.38 | 272 | 7.7 | 355 | 8.00 | |

a) In acetonitrile containing 0.1 M tetrabutylammonium perchlorate. b) In methanol. c) Rate constant for the reaction of the substrate with solvated electron in methanol.

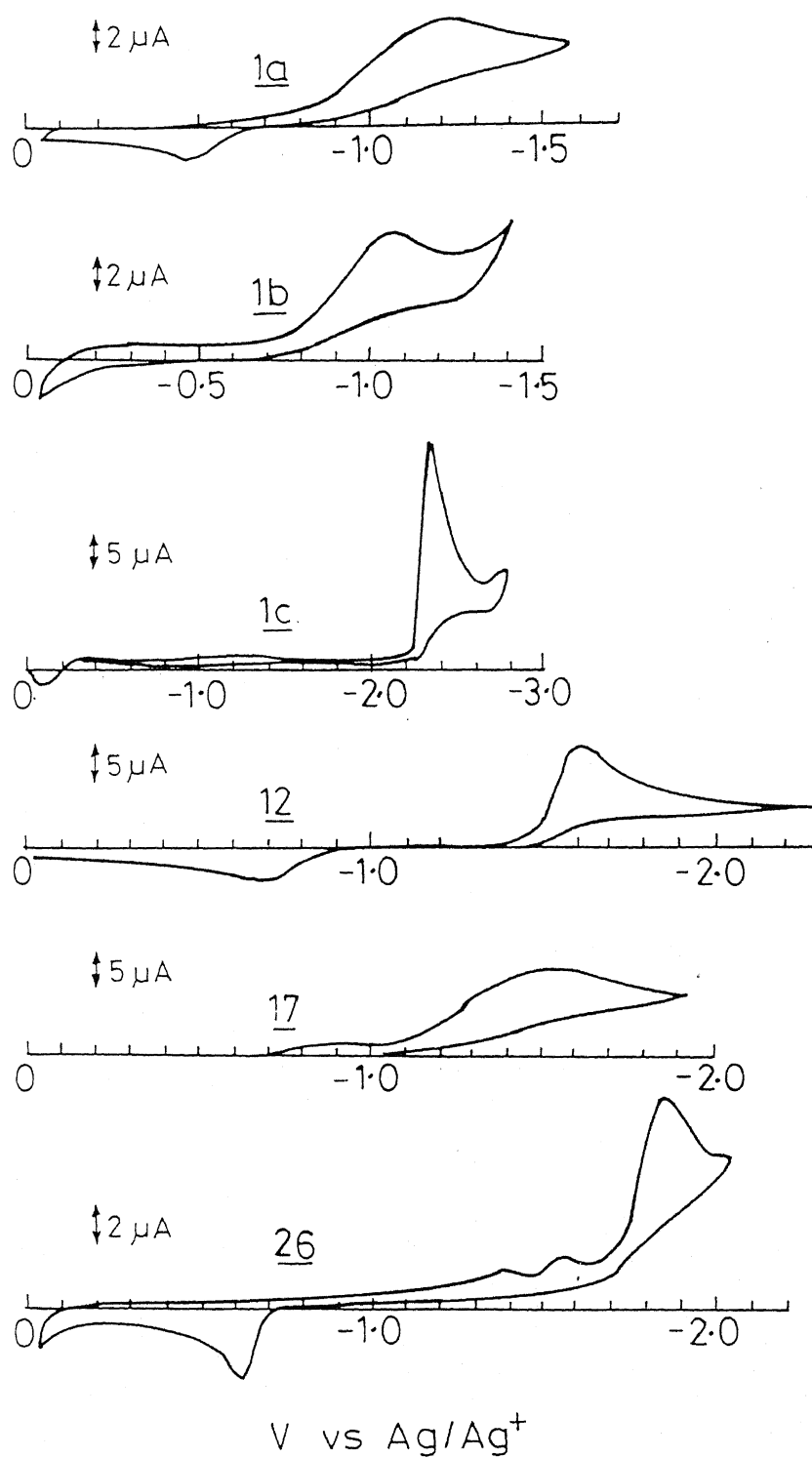


Figure I.1 Cyclic voltammograms of 1a-c, 12, 17 and 26

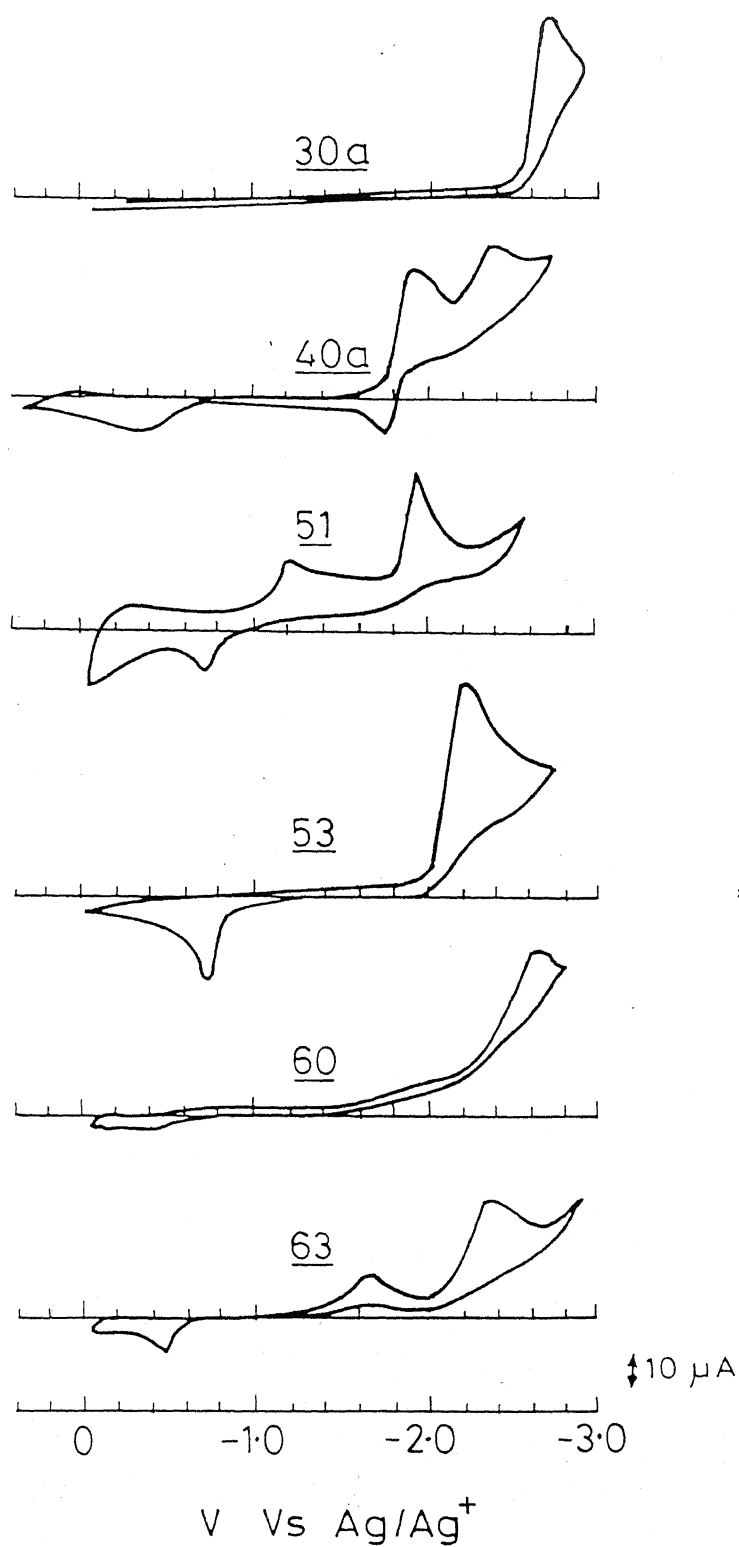


Figure I.2 Cyclic voltammograms of 30a, 40a, 51, 53, 60 and 63

requisite potentials, in each case and recording their absorption spectra. The spectral details, which are summarized in Tables I.1 and I.2, indicate that the starting substrates are characterized by an absorption maximum around 260-283 nm. The corresponding radical anions exhibited a red shifted absorption maximum around 345-425 nm; the radical anions of 30a-c exhibited an additional absorption band around 285-290 nm.

Since the reduction peak potentials of these substrates under investigation are greater than the reduction potential for oxygen ($E_p = -0.90$ V vs. SCE),^{7d} one would expect the quenching of the radical anions, derived from these substrates, by oxygen. Indeed, all the radical anions formed from these substrates were quenched by oxygen, as evidenced by the disappearance of their absorption bands, on bubbling oxygen gas through their solutions in acetonitrile. It is quite likely that these radical anions react with oxygen to give superoxide, which can then generate the different oxygenated products, observed in these reactions.

I.5 PULSE RADIOLYSIS STUDIES¹⁰

Earlier studies have shown that the radical anions of unsaturated organic compounds can be generated through their reactions with solvated electrons (e^-_{sol}) under pulse radiolytic conditions.^{11,12} In the present study, the radical

anions of Δ^2 -oxazolinones 1a-c and 12 and the bioxazolinodiones 17 and 26 were generated in methanol pulse radiolytically and their absorption spectra are presented in Figure I.3. These radical anions exhibited strong absorption maxima in the region of 295-350 nm and were shortlived in methanol ($\tau_{1/2} = 2.3-214 \mu s$). As is evident from Table I.1, these radical anions are formed from their appropriate precursors through the reaction with solvated electron under diffusion controlled rates.

I.6 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Beckman DB or Cary 219 spectrophotometers. The NMR traces were recorded on Varian EM-390 NMR spectrometer, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single-focussing mass spectrometer or a Varian Mat CH7, mass spectrometer at 70 eV. The petroleum ether used was the fraction with bp 60-80 °C. THF used was dried over sodium and was distilled immediately before use. Gold Label (Aldrich) acetonitrile was used for cyclic voltammetric studies and spectral grade methanol (Fischer Scientific) was used for pulse radiolysis.

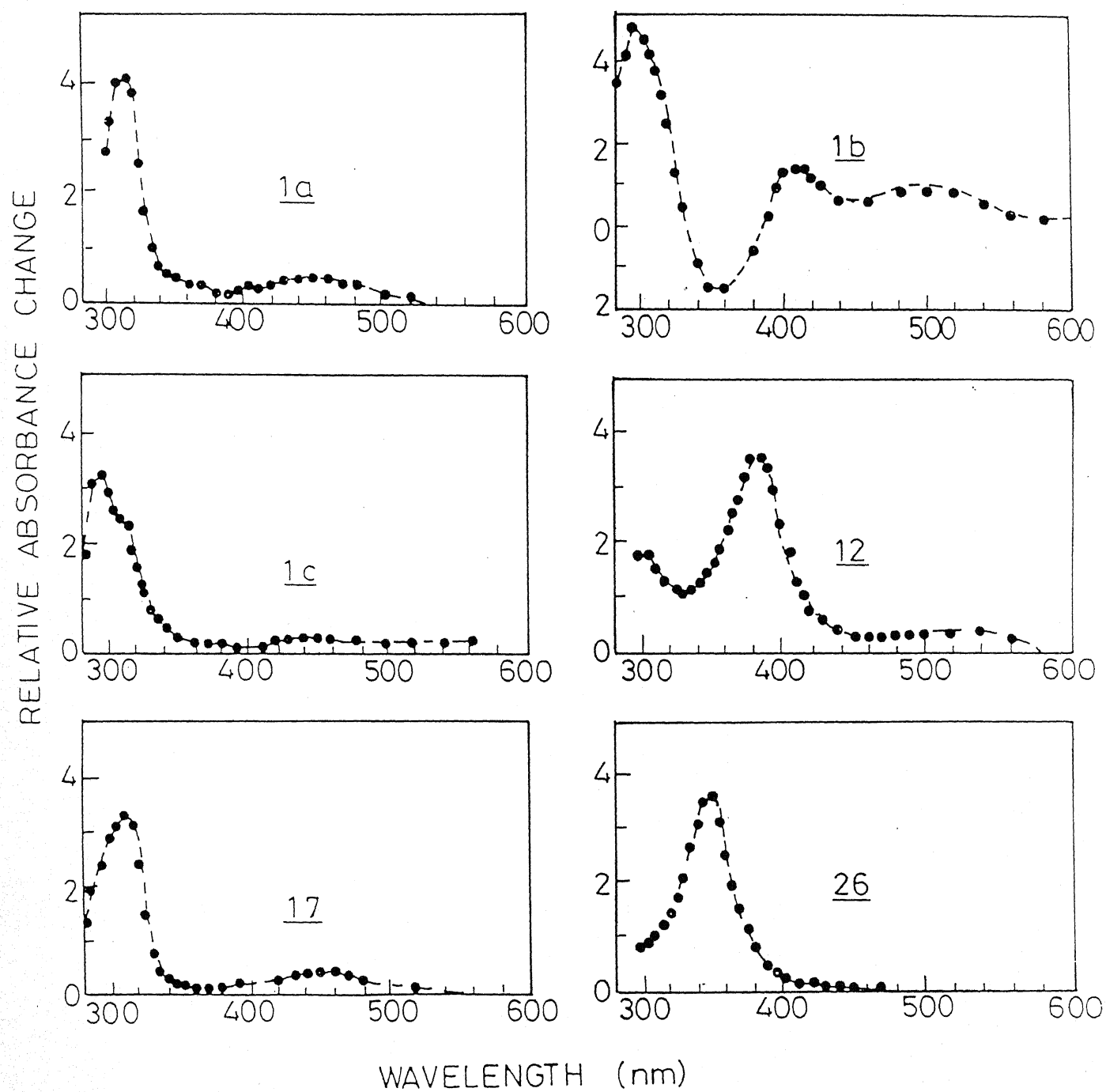


Figure I.3 Absorption spectra of the pulse radiolytically generated radical anions from 1a-c, 12, 17 and 26

I.6.1 Starting Materials. 2,4-Diphenyl- Δ^2 -oxazolin-5-one (1a),^{5b} mp 104-105 °C, 4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one (1b),¹³ mp 69-70 °C, 2,4,4-triphenyl- Δ^2 -oxazolin-5-one (1c),¹⁴ mp 136-137 °C, 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (12),¹⁵ mp 165-166 °C, bi-4,4'-(2,4-diphenyl- Δ^2 -oxazolin-5-one) (17),^{16,17} mp 193-194 °C, bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (26),^{16,17} mp 209-210 °C, 3,3,5-triphenyl-2(3H)-furanone (30a),¹⁸ mp 121 °C, 3-methyl-3,4,5-triphenyl-2(3H)-furanone (30b),¹⁹ mp 118-119 °C, 3,3,4,5-tetraphenyl-2(3H)-furanone (30c),²⁰ mp 137 °C, 1,3,3-triphenylprop-2-ene-1-one (40a),¹⁸ mp 92-93 °C, 3,4,5-triphenyl-2(5H)-furanone (53),²¹ mp 124-125 °C, 3-phenyl-2(3H)-benzofuranone (60),²² mp 113-114 °C, and 3,3'-diphenyl-3,3'-bibenzofuran-2,2'(3H,3'H)-dione (63),²³ mp 175-176 °C were prepared by reported procedures.

I.6.2 Reaction of 2,4-Diphenyl- Δ^2 -oxazolin-5-one (1a) with Potassium in THF. A mixture of 1a (1.2 g, 5.0 mmol) and finely cut potassium (0.39 g, 10 mmol) in dry THF (125 mL) was shaken in a Schlenk tube for 4 h. A few clean, broken glass pieces were added to the mixture to ensure a fresh surface of metal throughout the reaction. The reaction mixture underwent pronounced colour changes, indicative of the formation of radical anion intermediates. On completion of the reaction, the mixture was poured into moist THF (100 mL) to destroy

any unchanged potassium and the solvent was removed under vacuum. The residual solid was treated with water (10 mL) and extracted with ethyl acetate. Removal of the solvent from the organic layer gave a residual solid, which was fractionally crystallized from benzene to give 140 mg (12%) of dibenzamide (11a), mp 145 °C (mixture melting point).²⁴ The mother liquor after removal of 11a was evaporated under vacuum and the residual solid was recrystallized from ethanol to give 250 mg (33%) of C-phenylglycine (10a), mp 270-280 °C (mixture melting point).²⁵

The aqueous layer, on acidification with dilute hydrochloric acid, gave 350 mg (27%) of N-benzoyl-C-phenylglycine (6a), mp 177-178 °C (mixture melting point),^{5b} after recrystallization from ethanol.

Treatment of 1a (0.5 g, 2.1 mmol) with potassium (0.16 g, 4.1 mmol) in THF, saturated with oxygen for 10 h and workup as in the earlier case gave 190 mg (40%) of 11a (extraction of the reaction mixture with methylene chloride, chromatographing the residual solid over neutral alumina, elution with a mixture (4:6) of ethyl acetate and benzene and recrystallization from benzene), mp 145 °C (mixture melting point). Acidification of the aqueous layer with dilute hydrochloric acid gave 80 mg (30%) of benzoic acid (9), mp 120-121 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

I.6.3 Reaction of 4-Benzyl-2-phenyl- Δ^2 -oxazolin-5-one (1b) with Potassium in THF. A mixture of 1b (1.25 g, 5.0 mmol) and potassium (0.39 g, 10 mmol) in THF (125 mL) was shaken in a Schlenk tube for 4 h and workup of the mixture as in the earlier case by treatment with moist THF (100 mL) and removal of the solvent under reduced pressure gave a residual solid which was treated with water (10 mL) and extracted with ethyl acetate. Acidification of the aqueous layer with dilute hydrochloric acid gave 200 mg (32%) of benzoic acid (9), mp 120-121 °C.

Removal of the solvent from the organic layer gave a residual solid, which was fractionally crystallized from a mixture (1:9) of benzene and petroleum ether to give 300 mg (37%) of β -phenylalanine (10b), mp 284-288 °C (mixture melting point),¹⁵ after recrystallization from ethanol. The mother liquor was concentrated under vacuum to give a solid material, which was recrystallized from petroleum ether to give 70 mg (6%) of the unchanged starting material (1b), mp 69-70 °C (mixture melting point).

I.6.4 Reaction of 2,4,4-Triphenyl- Δ^2 -oxazolin-5-one (1c) with Potassium in THF. A solution of 1c (1.56 g, 5 mmol) in THF (125 mL) was shaken with potassium (0.39 g, 10 mmol) for 45 h. The colourless reaction mixture became light yellow and later turned to pale yellow. On completion of the reaction, the

solvent was removed under reduced pressure, treated the residue with water (10 mL) and extracted with methylene chloride.

Removal of the solvent from the organic layer gave 500 mg (30%) of N-benzoyl-C,C-diphenylglycine (6c), mp 166-167 °C (mixture melting point),¹⁴ after recrystallization from benzene.

Acidification of the aqueous layer with dilute hydrochloric acid gave 810 mg (57%) of N-benzoyl-C,C-diphenylmethanamine (5c), mp 191-192 °C (mixture melting point),¹⁴ after recrystallization from ethanol.

I.6.5 Reaction of 4-Benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (12) with Potassium in THF. A solution of 12 (1.15 g, 5 mmol) in dry THF (125 mL) was shaken with potassium (0.39 g, 10 mmol) for 3 h. The reaction mixture was worked up as in the earlier case to give a residual solid, which was treated with water and extracted with methylene chloride. The aqueous layer, on acidification with dilute hydrochloric acid gave a solid material, which was fractionally crystallized from ethanol to give 480 mg (39%) of N-benzoylaminocinnamic acid (15), mp 222-224 °C (mixture melting point).²⁶ The mother liquor on concentration gave 220 mg (39%) of benzoic acid (9), mp 120-121 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

Removal of the solvent from the organic layer gave 100 mg

(9%) of the unchanged starting material (12), mp 165-166 °C (mixture melting point), after recrystallization from ethanol.

I.6.6 Reaction of Bi-4,4'-(2,4-diphenyl- Δ^2 -oxazolin-5-one) (17) with Potassium in THF. A solution of 17 (0.94 g, 2.0 mmol) in dry THF (125 mL) was shaken with potassium (0.25 g, 6.4 mmol) for 5 h. The colour of the reaction mixture became yellow at first and later changed to red and finally, brown. The reaction mixture was poured into moist THF (100 mL) and the solvent was removed under vacuum. The residue was treated with water (10 mL) and extracted with ethyl acetate. Evaporation of the solvent from the ethyl acetate-extract gave a solid material, which was fractionally crystallized from benzene to give 150 mg (17%) of dibenzamide (11a), mp 145 °C (mixture melting point). The mother liquor on evaporation gave a solid, which was fractionally crystallized from ethanol to give 310 mg (41%) of 2,3,5,6-tetra-phenylpyrazine (25), mp 249-250 °C (mixture melting point)²⁷ and 80 mg (14%)⁴ of C-phenyglycine (10a), mp 270-280 °C (mixture melting point).

The aqueous layer was acidified with dilute hydrochloric acid and extracted with ethyl acetate to give 80 mg (8%)⁴ of N-benzoyl-C-phenyglycine (6a), mp 177-178 °C (mixture melting point), after recrystallization from ethanol.

I.6.7 Reaction of Bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (26) with Potassium in THF. A mixture of 26 (0.95 g, 1.9 mmol) and potassium (0.25 g, 6.4 mmol) in dry THF (125 mL) was shaken for 5 h and worked up as in the earlier cases to give a solid, which was treated with water (10 mL) and extracted with ethyl acetate (100 mL). Removal of the solvent from the ethyl acetate-extract gave a product, which was fractionally crystallized from benzene to give 200 mg (20%)⁴ of N-benzoylaminocinnamic acid (15), mp 222-224 °C (mixture melting point), and 50 mg (11%)⁴ of benzamide (29), mp 128-129 °C (mixture melting point). The mother liquor was concentrated to give a solid, which was recrystallized from methanol to give 150 mg (15%)⁴ of N-benzoyl- β -phenylalanine (6b), mp 186-187 °C (mixture melting point).¹⁵

I.6.8 Reaction of 2,4-Diphenyl- Δ^2 -oxazolin-5-one (1a) with Potassium Superoxide. A mixture of 1a (0.5 g, 2 mmol), potassium superoxide (0.29 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred at room temperature for 24 h, protected from light. The reaction mixture was poured into water (20 mL) and extracted with aqueous sodium chloride. The aqueous layer, on acidification with dilute hydrochloric acid gave 40 mg (7%) of N-benzoyl-C-phenylglycine (6a), mp 177-178 °C (mixture melting point).

Removal of the solvent from the organic layer gave 260 mg (55%) of dibenzamide (11a), mp 145 °C (mixture melting point).

I.6.9 Reaction of 4-Benzyl-2-phenyl- Δ^2 -oxazolin-5-one (1b) with Potassium Superoxide. A mixture of 1b (0.4 g, 1.6 mmol), potassium superoxide (0.22 g, 3.1 mmol), and 18-crown-6 (0.4 g, 1.6 mmol), in benzene (100 mL) was stirred at room temperature for 24 h, protected from light. The reaction mixture was poured into water (20 mL) and extracted with aqueous sodium chloride. The aqueous layer was acidified with dilute hydrochloric acid and extracted with ethyl acetate. Removal of the solvent under vacuum gave a solid, which on recrystallization from methanol gave 100 mg (23%) of N-benzoyl- β -phenylalanine (6b), mp 186-187 °C (mixture melting point). Concentration of the mother liquor gave a solid, which on recrystallization from a mixture (1:9) of benzene and petroleum ether gave 90 mg (46%) of benzoic acid (9), mp 120-121 °C (mixture melting point). Removal of the solvent from the benzene-extract gave a solid, which was recrystallized from benzene to give 80 mg (21%) of N-benzoylphenylacetamide (11b), mp 129-130 °C (mixture melting point).²⁸

I.6.10 Reaction of 2,4,4-Triphenyl- Δ^2 -oxazolin-5-one (1c) with Potassium Superoxide. A mixture of 1c (0.67 g, 2.1 mmol), potassium superoxide (0.56 g, 8 mmol) and 18-crown-6 (1 g,

4 mmol) was stirred at room temperature for 24 h. The reaction mixture was worked up as in the earlier cases by pouring into water (20 mL) and extracting with sodium chloride solution. Removal of the solvent from the organic layer gave 70 mg (10%) of the unchanged starting material (1c), mp 136-137 °C (mixture melting point), after recrystallization from ethanol. The aqueous layer, on acidification with dilute hydrochloric acid, gave 600 mg (85%) of N-benzoyl-C,C-diphenylglycine (6c), mp 166-167 °C (mixture melting point), after recrystallization from ethanol.

I.6.11 Reaction of Bi-4,4'-(4-benzyl,2-phenyl- Δ^2 -oxazolin-5-one) (26) with Potassium Superoxide. A mixture of 26 (0.5 g, 1.0 mmol), potassium superoxide (0.14 g, 2.0 mmol), and 18-crown-6 (0.26 g, 1.0 mmol) in benzene (100 mL) was stirred for 24 h. The reaction mixture was worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. The aqueous layer was acidified with dilute hydrochloric acid and extracted with ethyl acetate. Removal of the solvent gave a solid, which was fractionally crystallized from ethanol to give 150 mg (28%) of N-benzoylaminocinnamic acid (15), mp 186-187 °C (mixture melting point). The mother liquor on concentration gave 50 mg (21%)⁴ of benzoic acid (9), mp 120-121 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

Removal of the solvent from the benzene-extract gave 200 mg (40%) of the unchanged starting material (26), mp 209-210 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

I.6.12 Reaction of 3,3,5-Triphenyl-2(3H)-furanone (30a) with Potassium in THF, Saturated with Oxygen. A mixture of 30a (1.56 g, 5 mmol) and potassium (0.39 g, 10 mmol) in THF (125 mL), saturated with oxygen was shaken for 20 h and workup of the mixture as in the earlier cases by treatment with moist THF (50 mL) and removal of the solvent under vacuum gave a residual solid, which was treated with water and extracted with methylene chloride (100 mL). The aqueous layer was acidified with dilute hydrochloric acid and extracted with benzene. Removal of the solvent from the benzene layer gave 350 mg (57%) of benzoic acid (9), mp 120-121 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

Removal of the solvent from the methylene chloride-extract gave a product mixture, which was chromatographed over silica gel. Elution of the column with a mixture (1:9) of benzene and petroleum ether gave 210 mg (14%) of the unchanged starting material (30a), mp 121 °C (mixture melting point). Further elution of the column with a mixture (1:4) of benzene

and petroleum ether, followed by recrystallization from the same solvent gave 180 mg (13%) of 1,3,3-triphenylprop-2-ene-1-one (40a), mp 92 °C (mixture melting point).¹⁹ Subsequent elution of the silica gel column with a mixture (1:9) of ethyl acetate and benzene gave 180 mg (11%) of β -benzoyl- α,α -diphenylpropanoic acid (36a), mp 180 °C (mixture melting point), after recrystallization from a mixture (1:3) of benzene and petroleum ether.

In a repeat run, treatment of 30a (1.56 g, 5 mmol) with potassium (0.78 g, 20 mmol) for 10 h and workup as in the earlier cases gave 200 mg (33%) of 9, mp 120-121 °C (mixture melting point), 200 mg (13%) of the unchanged starting material (30a), mp 121 °C (mixture melting point), 110 mg (8%) of 40a, mp 92 °C (mixture melting point), and 190 mg (12%) of 36a, mp 180 °C (mixture melting point).

In a third run, 1.56 g (5 mmol) of 30a was treated with potassium (0.39 g, 10 mmol) in THF (125 mL), saturated with oxygen for 10 h and worked up as in the earlier case to give a solid, which was treated with water (10 mL) and extracted with methylene chloride (100 mL). Workup of the methylene chloride-extract gave 370 mg (22%) of the unchanged starting material (30a), mp 121 °C (mixture melting point), 205 mg (13%) of 40a, mp 92 °C (mixture melting point), and 190 mg (12%) of 36a, mp 180 °C (mixture melting point). Acidification of the aqueous layer with dilute hydrochloric acid gave 305 mg (49%) of benzoic acid (9), mp 120-121 °C (mixture melting point).

I.6.13 Reaction of 3-Methyl-3,4,5-triphenyl-2(3H)-furanone (30b) with Potassium in THF, Saturated with Oxygen. A solution of 30b (0.82 g, 2.5 mmol) in THF (125 mL) was shaken with potassium (0.2 g, 5 mmol) for 6 h and oxygen gas was bubbled through the reaction mixture for 20 minutes before workup. Removal of the solvent under vacuum gave a residual solid which was treated with water (10 mL) and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid and workup as in the earlier cases gave 240 mg (29%) of β -benzoyl- α,α -diphenyl- α -methylpropanoic acid (36b), mp 175 °C (mixture melting point),¹⁹ after recrystallization from a mixture (1:3) of benzene and petroleum ether, and 15 mg (5%) of benzoic acid (9), mp 120-121 °C (mixture melting point).

Removal of the solvent from the methylene chloride-extract gave a solid, which on recrystallization from ethanol gave 70 mg (9%) of the unchanged starting material (30b), mp 118-119 °C (mixture melting point). Concentration of the mother liquor gave a solid, which on recrystallization from a mixture (1:4) of benzene and petroleum ether gave 70 mg (9%) of 1,2,3-triphenylbut-2-ene-1-one (40b), mp 100-101 °C (mixture melting point).²⁹

I.6.14 Reaction of 3,3,4,5-Tetraphenyl-2(3H)-furanone (30c) with Potassium in THF, Saturated with Oxygen. A mixture

of 30c (0.97 g, 2.5 mmol) and potassium (0.2 g, 5 mmol) in THF (125 mL), saturated with oxygen was shaken for 8 h. On completion of the reaction, the solvent was removed under reduced pressure, treated the residue with water (10 mL) and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 250 mg (41%) of benzoic acid (9), mp 120-121 °C (mixture melting point).

Removal of the solvent from the methylene chloride-extract gave a product mixture which was chromatographed over silica gel. Elution of the column with a mixture (1:4) of benzene and petroleum ether gave 200 mg (21%) of the unchanged starting material (30c), mp 137 °C (mixture melting point), after recrystallization from a mixture (1:4) of benzene and petroleum ether. Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 90 mg (10%) of 1,2,3,3-tetraphenylprop-2-ene-1-one(40c), mp 152-153 °C (mixture melting point),³⁰ after recrystallization from a mixture (9:1) of benzene and petroleum ether.

Subsequent elution of the column with benzene gave 160 mg (15%) of 3,3,4,5-tetraphenyl-5-hydroxyfuran-2-one (39c), mp 178-179 °C, after recrystallization from a mixture (1:4) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3300 (OH), 3100, 3065 and 3030 (CH), 1755 (C=O), 1600 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol) : 240 nm (ϵ , 22,330), and 280 (365).

^1H NMR spectrum (CDCl_3) : δ 4.0 (s, 1 H, OH, D_2O -exchangeable), 4.6 (s, 1 H, methine), and 6.6 (m, 20 H, aromatic).

Mass spectrum, m/e (relatively intensity) : 406 (M^+ , 20), 388 (26), 360 (19), 359 (17), 344 (3), 311 (1), 283 (19), 267 (6), 265 (5), 255 (98), 254 (32), 253 (15), 252 (15), 239 (12), 210 (30), 178 (21), 177 (30), 152 (12), 139 (4), 105 (100), and 77 (60).

Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3$: C, 82.75; H, 5.21. Found: C, 83.25; H, 5.29.

I.6.15 Acid-Catalysed Conversion of 39c to 30c. Dry HCl gas was passed through a solution of 39c (0.2 mg, 5 mmol) in THF (10 mL) for 10 minutes. Removal of the solvent under vacuum gave a solid, which was recrystallized from a mixture (1:2) of benzene and petroleum ether to give 165 mg (82%) of 30c, mp 136–137 °C (mixture melting point).

I.6.16 Reaction of 1,3,3-Triphenylprop-2-ene-1-one (40a) with Potassium in THF, Saturated with Oxygen. A solution of 40a (1.42 g, 5 mmol) in THF (125 mL), saturated with oxygen was shaken with potassium (0.39 g, 10 mmol) for 10 h and worked up as in the earlier cases gave 60 mg (10%) of benzoic acid (9)

(acidification of the aqueous layer with dilute hydrochloric acid), mp 120-121 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

Removal of the solvent from the organic layer gave a product, which was chromatographed over silica gel. Elution with petroleum ether gave 70 mg (8%) of benzophenone (46), mp 49-50 °C (mixture melting point), after recrystallization from petroleum ether. Further elution with a mixture (1:9) of benzene and petroleum ether gave 659 mg (49%) of β,β -diphenylpropiophenone (45), mp 92 °C (mixture melting point).³¹ Continued elution of the silica gel column with a mixture (1:4) of benzene and petroleum ether gave 400 mg (28%) of the unchanged starting material (40a), mp 92 °C (mixture melting point).

I.6.17 Reaction of 2,2',3,3',4,4'-Hexaphenyl-2,2'-bifuran-5,5' (2H,2'H)-dione (51) with Potassium. A mixture of 51 (0.62 g, 1 mmol) and potassium (0.16 g, 4 mmol) in THF (125 mL) was shaken for 6 h. The reaction mixture was worked up as in the earlier cases to give a residual solid, which was treated with water and extracted with methylene chloride. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica gel. Elution of the column with a mixture (1:4) of benzene and petroleum ether gave 200 mg (32%) of 3,4,5-triphenyl-2(5H)-furanone (53), mp 124-125 °C (mixture melting point), after recrystallization

from methanol. Further elution with a mixture (1:1) of benzene and petroleum ether gave 140 mg (29%) of 2,3-diphenylpropenoic acid (59), mp 170-171 °C (mixture melting point), after recrystallization from ethanol.

The aqueous layer, on acidification with dilute hydrochloric acid, gave 55 mg (22%) of benzoic acid (9), mp 120-121 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

I.6.18 Reaction of 3,4,5-Triphenyl-2(5H)-furanone (53) with Potassium in THF, Saturated with Oxygen. A mixture of 53 (1.56 g, 5 mmol) and potassium (0.39 g, 10 mmol) in THF (125 mL), saturated with oxygen was shaken for 10 h and worked up as in the earlier cases to give a residual solid, which was treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a product mixture, which was chromatographed over silica gel. Elution of the column with a mixture (1:4) of benzene and petroleum ether gave 80 mg (5%) of the unchanged starting material (53), mp 124-125 °C (mixture melting point). Subsequent elution with benzene gave 540 mg (70%) of 2,3-diphenylpropenoic acid (59), mp 171 °C (mixture melting point).

Acidification of the aqueous layer with dilute hydrochloric acid gave 90 mg (15%) of benzoic acid (9), mp 120-121 °C (mixture melting point).

I.6.19 Reaction of 3-Phenyl-2(3H)-benzofuranone (60) with Potassium in THF, Saturated with Oxygen. Treatment of 60 (1.05 g, 5 mmol) with potassium (0.39 g, 10 mmol) in THF (125 mL), saturated with oxygen for 24 h and workup of the reaction mixture as in the earlier cases gave 600 mg (57%) of the unchanged starting material (60), mp 113-114 °C, (mixture melting point).

I.6.20 Reaction of 3,3'-Diphenyl-3,3'-bibenzofuran-2,2'(3H,3'H)-dione (63) with Potassium in THF. A mixture of 63 (0.5 g, 1.2 mmol) and potassium (0.1 g, 2.5 mmol) in THF (125 mL) was shaken for 10 h and workup of the mixture as in the earlier cases gave a solid, which was treated with water (10 mL) and extracted with methylene chloride (100 mL). Removal of the solvent gave 290 mg (58%) of the benzofuranone 60, mp 113-114 °C (mixture melting point).

I.6.21 Reaction of 3,3,5-Triphenyl-2(3H)-furanone (30a) with Potassium Superoxide. A mixture of 30a (0.94 g, 3 mmol), potassium superoxide (0.45 g, 6 mmol) and 18-crown-6 (0.8 g, 3 mmol) in benzene (100 mL) was stirred for 24 h. The reaction mixture was worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave a solid, which on recrystallization from or mixture (1:1) of benzene and petroleum ether gave 520 mg (52%) of β -benzoyl- α,α -diphenylpropanoic

acid (36a), mp 180-181 °C (mixture melting point). Concentration of the mother liquor gave a solid, which on recrystallization from a mixture (1:9) of benzene and petroleum ether gave 70 mg (19%) of benzoic acid (9), mp 120-121 °C (mixture melting point).

Removal of the solvent from the organic layer gave a mixture of 120 mg (13%) of the unchanged starting material (30a), mp 121 °C (mixture melting point), and 80 mg (9%) of 1,3,3-triphenylprop-2-ene-1-one (40a), mp 92 °C (mixture melting point).

I.6.22 Reaction of 3,3,4,5-Tetraphenyl-2(3H)-furanone (30c) with Potassium Superoxide. A mixture of 30c (0.49 g, 1.25 mmol), potassium superoxide (0.18 g, 2.5 mmol), and 18-crown-6 (0.33 g, 1.25 mmol) in benzene (100 mL) was stirred for 24 h, protected from light and worked up as in the earlier cases. The aqueous layer, on acidification with dilute hydrochloric acid gave 40 mg (25%) of benzoic acid (9), mp 120-121 °C (mixture melting point).

Removal of the solvent from the organic layer and workup as in the earlier cases gave 65 mg (13%) of the unchanged starting material (30c), mp 137 °C (mixture melting point), 30 mg (7%) of 1,2,3,3-tetraphenylprop-2-ene-1-one (40c), mp 152-153 °C (mixture melting point), and 260 mg (50%) of 3,3,4,5-tetraphenyl-5-hydroxyfuran-2-one (39c), mp 178-179 °C (mixture melting point).

I.6.23 Reaction of 1,3,3-Triphenylprop-2-ene-1-one (40a) with Potassium Superoxide. A mixture of 40a (0.29 g, 1 mmol), potassium superoxide (0.14 g, 2 mmol), and 18-crown-6 (0.26 g, 1 mmol) was stirred in benzene (100 mL) for 24 h and worked up as in the earlier cases. Removal of the solvent from the organic layer gave a product mixture, which was chromatographed over silica gel. Elution with petroleum ether gave 70 mg (38%) of benzophenone (46), mp 49-50 °C (mixture melting point). Further elution with a mixture (9:1) of benzene and petroleum ether gave 90 mg (30%) of the unchanged starting material (40a), mp 92 °C (mixture melting point).

I.6.24 Reaction of 3,4,5-Triphenyl-2(5H)-furanone (53) with Potassium Superoxide. Stirring a mixture of 53 (0.78 g, 2.5 mmol), potassium superoxide (0.36 g, 5 mmol), and 18-crown-6 (0.66 g, 2.5 mmol) in benzene for 24 h and workup as in the earlier cases, gave 50 mg (15%) of benzoic acid (9), mp 120-121 °C (mixture melting point) and 400 mg (70%) of 2,3-diphenylpropenoic acid (59), mp 171-172 °C (mixture melting point).

I.6.25 Cyclic Voltammetry. Cyclic voltammetric experiments were carried out using a Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat, a PAR Model 175 Universal Programmer and a Kipp and Zonen X-Y recorder. Experiments were performed in a standard three compartment cell equipped with a Pt-disc working

electrode, Pt-wire counter electrode and Ag/Ag^+ reference electrode. For spectroelectrochemical measurements, a specially designed cell was employed which consists of an extended 10 nm quartz cuvette, equipped with a Pt-gauze working electrode. The electrochemical experiments were carried out in acetonitrile solutions (~ 0.05 mM), under nitrogen atmosphere at controlled potentials and the absorption spectra of the electrochemically generated radical anions were recorded directly in a Cary 219 spectrophotometer. Electron reduction processes were monitored directly using a PAR 179 Digital Coulometer.

I.6.26 Pulse Radiolysis. The details of the computer controlled pulse radiolysis apparatus which allows determination of transient spectrum at various times after the pulse and kinetic measurements of the transients have been described elsewhere.³² The irradiation was carried out with 5 ns electron pulses from the Notre Dame 8 MeV ARCO LP-7 linear accelerator, using dose rates of $\sim 2 \times 10^{16}$ eV/g per pulse. The solutions of the appropriate substrates in methanol were deaerated before pulse radiolysis by bubbling nitrogen for at least 30 min and the deaeration was continued in the reservoir from which the solution was allowed to flow slowly and continuously through the cell. The rate constants for the reactions with solvated electrons (e^-_{sol}) were determined from the kinetic analysis of the enhanced rate of decay of e^-_{sol} in the presence of the appropriate substrate or from the growth rate of the radical anion.

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CHAPTER II

ELECTRON TRANSFER REACTIONS. REACTION OF SYDNONES WITH POTASSIUM

II.1 ABSTRACT

The reaction of several sydnones with potassium in THF has been investigated. The sydnones that we have studied include 3-p-tolyl-4-phenylsydnone (1a), 3,4-diphenylsydnone (1b), 3-p-anisyl-4-phenylsydnone (1c), 3-p-tolylsydnone (1d), 3-p-tolyl-4-methylsydnone (1e), and 3-phenylsydnone (1f). The reaction of 1a with potassium in THF, for example, gave a mixture of phenylglyoxylic acid p-tolylhydrazone (4a, 31%), p-toluidine (13a, 11%), benzoic acid (14a, 3%), N-benzoyl-p-toluidine (15a, 14%), 1,2-bisphenylazodi(p-tolyl)ethylene (16a, 2%), and 4,4'-dimethylazobenzene (17a, 2%). A higher yield of benzoic acid (14a, 24%) was obtained, along with 4a (15%), 13a (13%) and 17a (1%), when the reaction of 1a with potassium was carried out in THF, saturated with oxygen. A similar mixture of products consisting of 4a (20%), 13a (19%), 14a (17%), and 15a (5%) was obtained when the reaction of 1a was carried out with potassium superoxide. Similarly, the

reaction of 1b with potassium in THF gave a mixture of phenylglyoxylic acid phenylhydrazone (4b, 31%), aniline (13b, 12%), benzoic acid (14a, 3%), benzanilide (15b, 15%), 1,2-bisphenylazostilbene (16b, 2%), and azobenzene (17b, 1%), whereas the reaction of 1c with potassium in THF gave a mixture of p-anisidine (13c, 17%), benzoic acid (14a, 10%), N-benzoyl-p-anisidine (15c, 20%), and 4,4'-dimethoxyazobenzene (17c, 2%). In contrast, the reaction of 1d with potassium gave a mixture of N-nitroso-N-p-tolylglycine (5d, 7%), p-toluidine (13a, 26%), and 4,4'-dimethylazobenzene (17a, 1%). Similarly, the reaction of 1e with potassium in THF gave a mixture of N-nitroso-N-p-tolylalanine (5e, 24%), p-toluidine (13a, 24%), N-acetyl-p-toluidine (15e, 20%), and 4,4'-dimethylazobenzene (17a, 2%). Similar product mixtures were obtained in the potassium superoxide oxidation of some of these substrates.

Reasonable mechanisms, involving the initial formation of radical anion intermediates and their further transformations to give the observed products have been suggested. Cyclic voltammetric studies have been carried out to measure the reduction potentials of 1a-f in the generation of their radical anions. The radical anions of 1a-f were also generated pulse radiolytically in methanol and their spectra showed absorption maxima in the region 340-480 nm.

II.2 INTRODUCTION

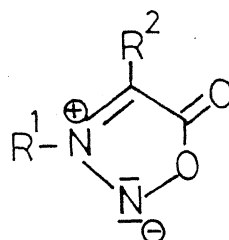
In Chapter I of this thesis, we have reported the results

of our studies on the reaction of Δ^2 -oxazolinones and bioxazolinediones with potassium in THF. In continuation of these studies, we have investigated the potassium induced transformations of some representative sydnones,¹ to examine the type of products formed in these reactions and also their reaction pathways.

II.3 RESULTS AND DISCUSSION

The sydnones that we have examined in the present studies include 3-p-tolyl-4-phenylsydnone (1a), 3,4-diphenylsydnone (1b), 3-p-anisyl-4-phenylsydnone (1c), 3-p-tolylsydnone (1d), 3-p-tolyl-4-methylsydnone (1e), and 3-phenylsydnone (1f) (Chart II.1).

The reaction of 1a with potassium in THF, for example, gave a mixture of phenylglyoxylic acid p-tolylhydrazone (4a, 31%), p-toluidine (13a, 11%), benzoic acid (14a, 3%), N-benzoyl-p-toluidine (15a, 14%), 1,2-bisphenylazodi(p-tolyl)ethylene (16a, 2%), and 4,4'-dimethylazobenzene (17a, 2%). When the reaction of 1a was carried out with potassium in THF, saturated with oxygen, a much higher yield of benzoic acid (14a, 24%) was obtained, along with 4a (15%), 13a (13%), and 17a (1%). Similarly, the reaction of 1b with potassium in THF gave a mixture of phenylglyoxylic acid phenylhydrazone (4b, 31%), aniline (13b, 12%), benzoic acid (14a, 3%), benzanilide

Chart II.1

1 a-f

- a) $R^1 = \text{p-CH}_3\text{C}_6\text{H}_4$; $R^2 = \text{C}_6\text{H}_5$
 b) $R^1 = R^2 = \text{C}_6\text{H}_5$
 c) $R^1 = \text{p-CH}_3\text{OC}_6\text{H}_4$; $R^2 = \text{C}_6\text{H}_5$
 d) $R^1 = \text{p-CH}_3\text{C}_6\text{H}_4$; $R^2 = \text{H}$
 e) $R^1 = \text{p-CH}_3\text{C}_6\text{H}_4$; $R^2 = \text{CH}_3$
 f) $R^1 = \text{C}_6\text{H}_5$; $R^2 = \text{H}$

(15b, 15%), 1,2-bisphenylazostilbene (16b, 2%), and azobenzene (17b, 1%). Under analogous conditions, 1c gave a mixture of p-anisidine (13c, 17%), benzoic acid (14a, 10%), N-benzoyl-p-anisidine (15c, 20%), and 4,4'-dimethoxyazobenzene (17c, 2%). In the reaction of 3-p-tolylsydnone (1d) with potassium in THF, likewise, a mixture of N-nitroso-N-p-tolylglycine (5d, 7%), p-toluidine (13a, 26%), and 4,4'-dimethylazobenzene (17a, 1%) was obtained. A similar mixture of products consisting of 5d (11%), 13a (15%) and 17a (1%) was obtained, when 1d was treated with potassium in THF, saturated with oxygen, under analogous conditions. The reaction of 1e with potassium in THF gave a mixture of 17a (2%), 13a (24%), N-acetyl-p-toluidine (15e, 20%) and N-nitroso-N-p-tolylalanine (5e, 24%), whereas, the reaction of 1e with potassium in THF, saturated with oxygen, under analogous conditions, gave a mixture of 5e (29%), 13a (11%), and 17a (2%). Similarly, the reaction of 3-phenylsydnone (1f) with potassium gave a mixture of N-nitroso-N-phenylglycine (5f, 14%), aniline (13b, 24%), and azobenzene (17b, 1%). A similar mixture of products consisting of 5f (27%), 13b (17%), and 17b (1%) was obtained when the reaction of 1e with potassium was carried out in THF, saturated with oxygen. The structures of all the products were determined on the basis of analytical results, spectral data and comparison with authentic samples, wherever possible.

The formation of the different products in the reaction of 1a-f with potassium in THF can be understood in terms of the reaction pathways shown in Scheme II.1. It has been assumed that the initial step in the reaction of 1a-f with potassium is an electron transfer process, leading to the radical anion intermediates 2a-f, which could undergo ring opening and further reorganization to give the new radical anion intermediates 3a-f. The formation of products such as 4a,b from 1a,b could be understood in terms of the reactions of 3a,b, through hydrogen atom abstraction from the solvent. The radical anion intermediates 3a-f can also transfer an electron back to the substrate (1a-f) or any other intermediate to give the zwitterionic species 7, which can then lose CO_2 to give the nitrile imine 8, which is isoelectronic with the azocarbene intermediate 11. The formation of products such as 16a,b can be understood in terms of the dimerization of 11, whereas the arylazo compounds 17a-c could arise through the dimerization of the nitrene intermediate 12, which in turn, is formed from 8.

A second possible mode of transformation of the radical anion intermediates 2a-f is their further reduction to give the dianion intermediates 6a-f, which can subsequently combine with oxygen, under workup conditions to give ultimately products such as 13a-c, 14a and 15a-c,e, as shown in Scheme II.1. The formation of the N-nitroso acids 5d-f, however, could be

understood in terms of the hydrolysis of the starting sydnone 1d-f, under the conditions of workup.

To examine the type of products formed in the reaction of sydnones with superoxide and also to see whether these products correspond to those formed on treatment of sydnones with potassium in THF and also with potassium in THF, saturated with oxygen, we have carried out the reactions of few representative sydnones such as 1a, 1d and 1e with potassium superoxide in benzene, containing 18-crown-6. The reaction of 1a with potassium superoxide, for example, gave a mixture of 4a (20%), 13a (19%), 14a (17%), and 15a (5%), along with some recovered starting material (1a, 28%). Similarly, the reaction of 1d with potassium superoxide gave a mixture of 5d (9%), 13a (26%), and 17a (2%), along with some recovered starting material (1d, 19%). Likewise, the reaction of 1e with potassium superoxide gave a mixture of 5e (11%), 13a (20%), and 17a (9%) and an appreciable quantity of the unchanged starting material (1e, 36%).

It is interesting to note that the products formed in the reactions of 1a,d,e with potassium superoxide are not significantly different from those obtained in the reaction of these substrates with potassium in THF, saturated with oxygen. It is quite likely that in the reaction of sydnones (1a,d,e) with potassium superoxide, the initial step involves

an electron transfer reaction to give the corresponding radical anions (2a,d,e), which in turn, may be undergoing further transformations, as shown in Scheme II.1. A further possible pathway involves a direct nucleophilic attack of the superoxide anion on the starting sydnones (1a,d,e) to give the corresponding hydroperoxy radical intermediates, analogous to 9(a,d,e), which in turn may lead to products such as 13a, 14a and 15a (Scheme II.1).

II.4 CYCLIC VOLTAMMETRIC STUDIES²

Earlier studies from this laboratory^{3,4} had highlighted the importance of electrochemical investigations in the generation and characterization of radical anions, the primary intermediates involved in the reaction of several unsaturated substrates with potassium in THF. In the present investigation, we have generated electrochemically the radical anions of 1a-f, the substrates under study. The cyclic voltammograms of 1a-f are shown in Figure II.1 and the reduction and oxidation potentials are summarized in Table II.1. The sydnones 1a-f exhibited reversible reduction peaks in the region of -1.60 to -1.95 V vs SSCE. It may be pointed out in this connection that the polarographic reduction of a few sydnones has been reported earlier in the literature.⁵ Thus, it has been shown that sydnones are reduced in alkaline solutions (pH > 7.5) to give hydrazoic acid,

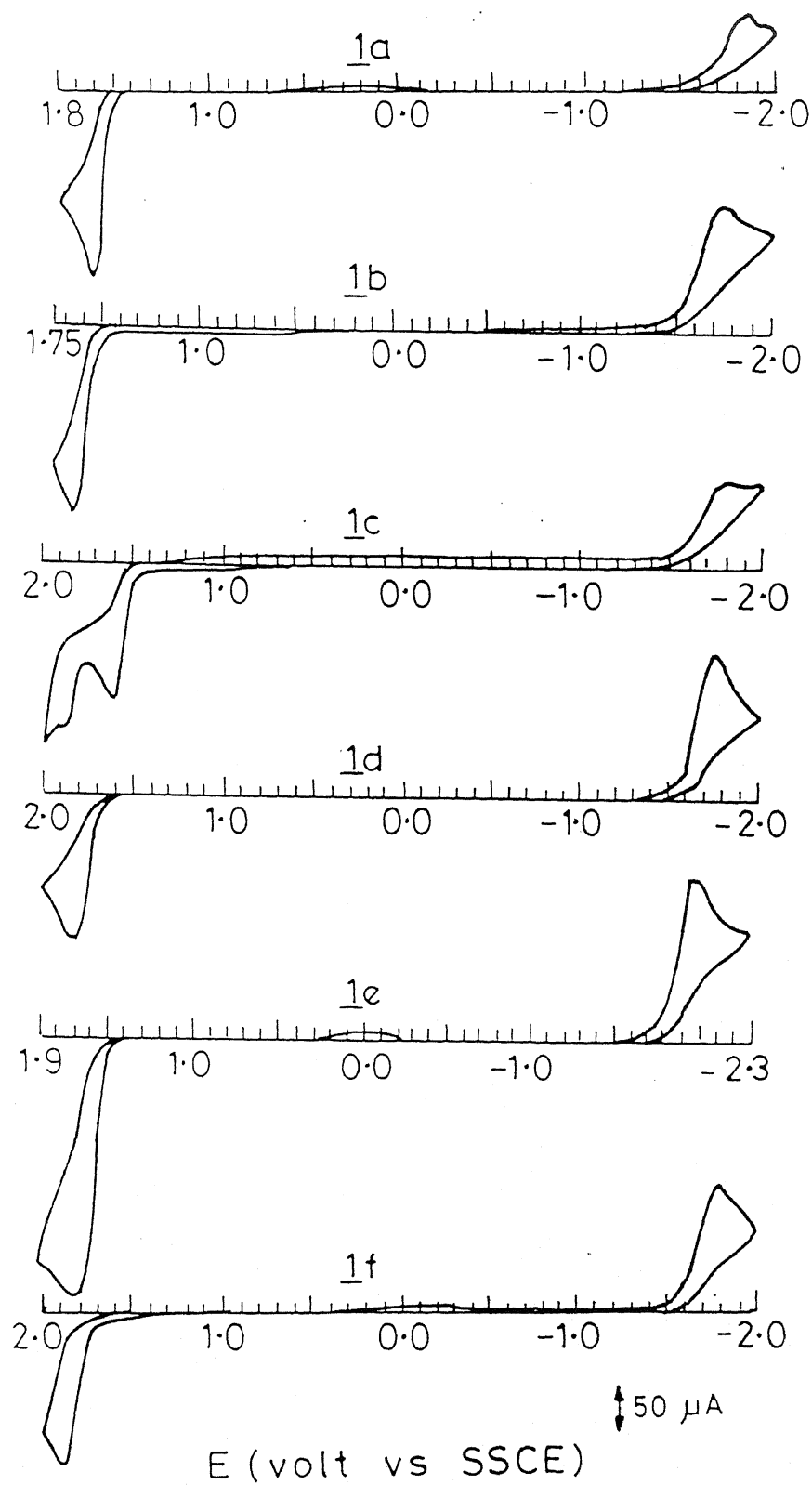


Figure II.1 Cyclic voltammograms of 1a-f

Table II.1 Electrochemical, spectral and kinetic data of 1a-f

| Substrate | Electrochemical ^a | | Absorption maxima ^b of radical anion (nm) | $k^{b,c}$ $10^4 \text{M}^{-1} \text{s}^{-1}$ (± 0.3) | $\tau_{1/2}^b$ μs (± 0.2) |
|-----------|------------------------------|---------------------------------------|---|--|--|
| | $E_p/2$ (oxidation) | $E_p/2$ (reduction) (V vs SSCE) | | | |
| <u>1a</u> | 1.60 | -1.65 | 420 | 1.7 | 1.3 |
| <u>1b</u> | 1.57 | -1.61 | 340, 425 | 1.5 | 2.1 |
| <u>1c</u> | 1.53, 1.82 | -1.72 | 410 | 1.6 | 0.9 |
| <u>1d</u> | 1.74 | -1.67 | 345, ~480 | 1.8 | 3.3 |
| <u>1e</u> | 1.57 | -1.90 | 340, ~480 | 1.4 | 2.2 |
| <u>1f</u> | 1.78 | -1.60 | 345, ~470 | 1.9 | 5.1 |

a) In acetonitrile containing 0.1 M tetrabutylammonium perchlorate. b) In methanol. c) Rate constant for the reaction between solvated electron and the substrate in methanol.

whereas, reduction of sydnones in acidic solutions ($\text{pH} < 6$) give amino acid derivatives.

II.5 PULSE RADIOLYSIS STUDIES⁶

Pulse radiolysis experiments were carried out using la-f, the substrates under investigation, to characterize the corresponding radical anions. As reported earlier,^{4,7-9} the radical anions of unsaturated organic compounds can be generated through the reaction with solvated electron (e^-_{sol}) in polar solvents such as methanol, under pulse radiolytic conditions. The absorption spectra of the different radical anions generated from la-f are presented in Figure II.2. These radical anions exhibited absorption maxima in the region of 340-480 nm. The lifetimes of these radical anions in methanol varied from 0.9 μs to 5.1 μs . The values of the rate constants for the reaction of the substrates (la-f) with the solvated electron (Table II.1) reveal that they were formed at diffusion controlled rates.

II.6 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or 580 infrared spectrophotometers. The electronic spectra were recorded on a Cary 219 spectrophotometer.

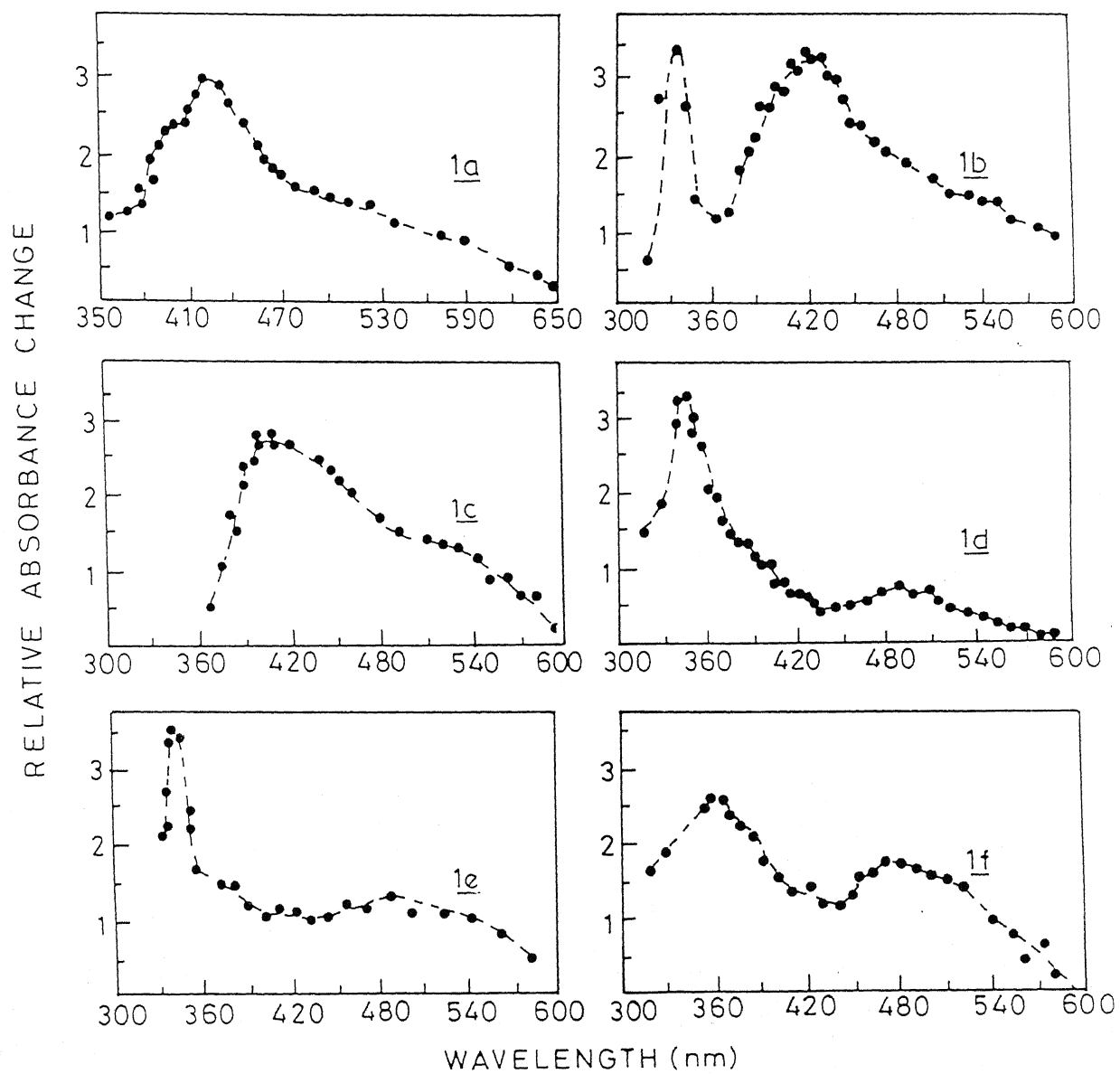


Figure II.2 Absorption spectra of the pulse radiolitically generated radical anions of 1a-f

¹H NMR spectra were recorded on a EM-390 NMR spectrometer. The mass spectra were recorded on a Varian Mat CH7 or a Hitachi RMU-6⁺ single-focussing mass spectrometer at 70 eV. The petroleum ether used was the fraction with bp 60-80 °C. THF used was dried over sodium and was distilled before use. Gold Label (Aldrich) acetonitrile was used for cyclic voltammetric studies and spectral grade methanol (Fischer Scientific) was used for pulse radiolysis experiments.

II.6.1 Starting Materials. 3-p-Tolyl-4-phenylsydnone (1a),¹⁰ mp 151-152 °C, 3,4-diphenylsydnone (1b),¹⁰ mp 184-185 °C, 3-p-tolylsydnone (1d),¹⁰ mp 144-145 °C, 3-p-tolyl-4-methylsydnone (1e),¹¹ mp 166-167 °C and 3-phenylsydnone (1f),¹² mp 134-135 °C were prepared by reported procedures.

II.6.2 Preparation of 3-p-Anisyl-4-phenylsydnone. A mixture of p-anisidine (20 g, 0.16 mol), methyl α -bromophenylacetate (37 g, 0.16 mol) and sodium acetate (13 g, 0.16 mol) in ethanol (30 mL) was refluxed for 24 h and treated with water to give methyl α -N-p-anisidylphenylacetate (40 g, 82%), mp 186-187 °C, after recrystallization from ethanol. Hydrolysis of this ester (40 g, 0.15 mol) by refluxing in 10% alcoholic sodium hydroxide solution (100 mL water and 30 mL ethanol) for

2 h, followed by acidification with dilute hydrochloric acid gave N-p-anisyl-C-phenylglycine (30 g, 79%), mp 170-171 °C, after recrystallization from ethanol. This glycine derivative (30 g, 0.12 mol) was dissolved in 50% hydrochloric acid (200 mL) and sodium nitrite (22 g, 0.32 mol) was added to it, in small portions, with stirring at 0 °C. The stirring was continued for 2 h and the organic material was extracted with ether (200 mL), washed with water and dried over anhydrous calcium chloride. Acetic anhydride (125 mL) was added to the ether solution and heated on a water bath for 3 h. After removing all the ether under vacuum, the reaction mixture, on cooling, was poured over crushed ice to give 18 g (78%) of 3-p-anisyl-4-phenylsydnone (1c), mp 129-130 °C, after recrystallization from a mixture (1:2) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3030, 2980 (CH), 1720 (C=O), and 1600 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 270 nm (ϵ , 4,690) and 370 (6,365).

^1H NMR spectrum (CDCl_3): δ 3.9 (s, 3 H, methoxy) and 7.0-7.7 (m, 9 H, aromatic).

Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3$: C, 67.16; H, 4.47; N, 10.44. Found: C, 66.85; H, 4.23; N, 10.83.

II.6.3 Reaction of 3-p-Tolyl-4-phenylsydnone (1a) with Potassium in THF. A solution of 1a (1.27 g, 5 mmol) in THF (125 mL) was shaken with potassium (0.39 g, 10 mmol) in a Schlenk tube for 6 h. Few broken glass pieces were added to the mixture to ensure a fresh surface of the metal throughout the reaction. The reaction mixture underwent pronounced colour change, indicative of the radical anion formation. On completion of the reaction, the mixture was drained into moist THF (100 mL) to destroy and unchanged potassium and the solvent was removed under reduced pressure to give a solid, which was treated with water (10 mL) and extracted with methylene chloride. The aqueous layer was acidified with dilute hydrochloric acid to give a solid, which was fractionally crystallized from a mixture (2:1) of benzene and petroleum ether to give 390 mg (31%) of phenylglyoxylic acid p-tolylhydrazone (4a), mp 163-164 °C.

IR spectrum ν_{\max} (KBr): 3220 (NH), 3200-2500 (OH), 1650 (C=O), and 1600 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 230 nm (ϵ , 12,700), 300 (8,400), and 350 (15,600).

^1H NMR spectrum (CDCl_3): δ 2.3 (s, 3 H, methyl), 6.7-7.8 (m, 9 H, aromatic), 8.3 (s, 1 H, NH, D_2O -exchangeable), and 11.3 (s, 1 H, OH, D_2O -exchangeable).

Mass spectrum, m/e (relative intensity): 254 (M^+ , 58),

235 (6), 211 (3), 210 (10), 209 ($M^+ - CO_2H$, 8), 208 (16), 207 (2), 194 (2), 107 (13), 106 (71), 105 (100), 104 (29), and 103 (8).

Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.87; H, 5.51; N, 11.02. Found: C, 71.11; H, 5.63; N, 11.42.

The mother liquor, on concentration gave a solid, which was recrystallized from a mixture (1:9) of benzene and petroleum ether to give 20 mg (3%) of benzoic acid (14a), mp 120-121 °C (mixture melting point).

Removal of the solvent from the methylene chloride-extract gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 15 mg (2%) of 4,4'-dimethylazobenzene (17a), mp 142-143 °C (mixture melting point).¹³ Further elution with a mixture (1:9) of benzene and petroleum ether gave 42 mg (2%) of 1,2-bisphenylazodi-(p-tolyl)ethylene (16a), mp 158-159 °C (mixture melting point).

IR spectrum ν_{max} (KBr): 3060, 2980 (CH), 1600 and 1580 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol): 270 nm (ϵ , 20,600), 290 (17,040), and 300 (12,500).

1H NMR spectrum ($CDCl_3$): δ 2.4 (s, 6 H, methyl) and 7.2-8.3 (m, 18 H, aromatic).

Anal. Calcd for $C_{28}H_{24}N_4$: C, 80.77; H, 5.77; N, 13.46.
Found: C, 80.39; H, 5.57; N, 13.05.

Continued elution of the column with a mixture (1:9) of benzene and petroleum ether gave 60 mg (11%) of p-toluidine (13a), mp 43-44 °C (mixture melting point), after recrystallization from petroleum ether. Further elution with a mixture (2:3) of benzene and petroleum ether gave 152 mg (14%) of N-benzoyl-p-toluidine (15a), mp 157-158 °C (mixture melting point),¹⁴ after recrystallization from aqueous ethanol. Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 150 mg (12%) of the unchanged starting material (1a), mp 151-152 °C (mixture melting point), after recrystallization from ethanol.

In a repeat run, 1.27 g (5 mmol) of 1a was treated with 0.78 g (20 mmol) of potassium in THF (125 mL) for 8 h and worked up as in the earlier case to give a mixture of 300 mg (23%) of 4a, mp 163-164 °C, 60 mg (10%) of 14a, mp 120-121 °C (mixture melting point), 15 mg (2%) of 17a, mp 143-144 °C (mixture melting point), 200 mg (37%) of 13a, mp 42-43 °C (mixture melting point), and 40 mg (4%) of 15a, mp 157-158 °C (mixture melting point).

In a third run, a solution of 1a (1.27 g, 5 mmol) in THF (125 mL), saturated with oxygen was shaken with potassium

(0.39 g, 10 mmol) for 40 h and the reaction mixture was worked up as in the earlier cases to give a mixture of 190 mg (15%) of 4a, mp 163-164 °C 10 mg (1%) of 17a, mp 142-143 °C (mixture melting point), 150 mg (24%) of 14a, mp 120-121 °C (mixture melting point), 70 mg (13%) of 13a, mp 42-43 °C (mixture melting point), and 560 mg (44%) of the recovered starting material (1a), mp 151-152 °C (mixture melting point).

II.6.4 Reaction of 3,4-Diphenylsydnone (1b) with Potassium in THF. Treatment of 1b (1.2 g, 5 mmol) with potassium (0.39 g, 10 mmol) in THF (125 mL) for 6 h and workup by pouring into moist THF and removal of the solvent under vacuum gave a residual solid, which was treated with water and extracted with methylene chloride as in the earlier cases. Acidification of the aqueous layer with dilute hydrochloric acid gave a solid, which was fractionally crystallized from a mixture (2:1) of benzene and petroleum ether to give 375 mg (32%) of phenylglyoxylic acid phenylhydrazone (4b) mp 161-162 °C (mixture melting point).¹⁵ Concentration of the mother liquor, after the removal of 4b, gave a solid, which on crystallization from a mixture (1:9) of benzene and petroleum ether gave 20 mg (3%) of benzoic acid (14a), mp 120-121 °C (mixture melting point).

Removal of the solvent from the organic layer gave a residue, which was chromatographed over neutral alumina. Elution with petroleum ether gave 10 mg (1%) of azobenzene (17b), mp 67-68 °C (mixture melting point),¹⁶ after recrystallization from petroleum ether. Further elution of the column with a mixture (1:9) of benzene and petroleum ether gave 40 mg (2%) of 1,2-bisphenylazostilbene (16b), mp 178-179 °C (mixture melting point). Subsequent elution with a mixture (1:9) of benzene and petroleum ether gave 55 mg (12%) of aniline (13b) (superimposable IR spectrum with that of an authentic sample). Further elution with a mixture (2:3) of benzene and petroleum ether gave 145 mg (15%) of benzanilide (15b), mp 160-161 °C (mixture melting point), after recrystallization from ethanol. Continued elution with a mixture (1:1) of benzene and petroleum ether gave 140 mg (12%) of the unchanged starting material (1b), mp 184-185 °C (mixture melting point), after recrystallization from ethanol.

II.6.5 Reaction of 3-p-Anisyl-4-phenylsydnone (1c) with Potassium in THF. A mixture of 1c (1.3 g, 5 mmol) and potassium (0.39 g, 10 mmol) in THF (125 mL) was shaken for 10 h and worked up as in the earlier cases by treatment with moist THF and removal of the solvent under vacuum. The residual

solid was treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 60 mg (10%) of benzoic acid (14a), mp 120-121 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

Removal of the solvent from the organic layer gave a residual solid, which was chromatographed over alumina. Elution with petroleum ether gave 20 mg (2%) of 4,4'-dimethoxyazobenzene (17c), mp 142-143 °C (mixture melting point).¹⁷ Further elution with a mixture (1:9) of benzene and petroleum ether gave 100 mg (17%) of *p*-anisidine (13c), mp 59-60 °C (mixture melting point), after recrystallization from aqueous ethanol. Subsequent elution with a mixture (2:3) of benzene and petroleum ether gave 220 mg (20%) of *N*-benzoyl-*p*-anisidine (15c), mp 153-154 °C (mixture melting point), after recrystallization from aqueous ethanol. Continued elution with a mixture (1:1) of benzene and petroleum ether gave 200 mg (15%) of the unchanged starting material (1c), mp 119-120 °C.

II.6.6 Reaction of 3-*p*-Tolylsydnone (1d) with Potassium in THF. A solution of 1d (1.76 g, 10 mmol) in THF (125 mL) was shaken with potassium (0.39 g, 10 mmol) for 12 h. On completion of the reaction, the solvent was removed under vacuum and

the residue was treated with water (10 mL), followed by extraction with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 140 mg (7%) of N-nitroso-N-p-tolyglycine (5d), mp 105-106 °C (mixture melting point),¹⁰ after recrystallization from ethanol. Removal of the solvent from the organic layer gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 20 mg (1%) of 4,4'-dimethylazobenze (17a), mp 142-143 °C (mixture melting point), after recrystallization from petroleum ether. Further elution of the column with a mixture (1:9) of benzene and petroleum ether gave 275 mg (26%) of p-toluidine (13a), mp 43-44 °C (mixture melting point). Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 650 mg (37%) of the unchanged starting material (1d), mp 144-145 °C (mixture melting point), after recrystallization from ethanol.

In a repeat run, treatment of 1d (1.7 g, 10 mmol) with potassium (0.39 g, 10 mmol) in THF (125 mL), saturated with oxygen for 10 h and workup as in the earlier cases gave 200 mg (11%) of 5d, mp 105-106 °C (mixture melting point), 20 mg (1%) of 17a, mp 142-143 °C (mixture melting point), 150 mg (15%) of 13a, mp 42-43 °C (mixture melting point), and 650 mg (37%) of the unchanged starting material (1d), mp 144-145 °C.

II.6.7 Reaction of 3-p-Tolyl-4-methylsydnone (1e) with Potassium in THF. Treatment of 1e (0.95 g, 5 mmol) with potassium (0.39 g, 10 mmol) in THF (125 mL) for 8 h as in the earlier cases and workup by treatment with moist THF and removal of the solvent under vacuum gave a residual solid, which was treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 250 mg (24%) of N-nitroso-N-p-tolyl-alanine (5e), mp 109-110 °C (mixture melting point),¹¹ after recrystallization from ethanol.

Removal of the solvent under vacuum from the methylene chloride-extract gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 20 mg (2%) of 4,4'-dimethylazobenzene (17a), mp 142-143 °C (mixture melting point). Further elution with a mixture (1:9) of benzene and petroleum ether gave 130 mg (24%) of p-toluidine (13a), mp 42-43 °C (mixture melting point), after recrystallization from petroleum ether. Subsequent elution of the column with a mixture (2:3) of benzene and petroleum ether gave 150 mg (20%) of N-acetyl-p-toluidine (15e), mp 154-155 °C (mixture melting point),¹⁴ after recrystallization from ethanol. Continued elution with a mixture (3:2) of benzene and petroleum ether gave 100 mg (11%) of the recovered starting material (1e),

mp 166-167 °C (mixture melting point), after recrystallization from ethanol.

In a repeat run, 0.95 g (5 mmol) of 1e was treated with 0.39 g (10 mmol) of potassium in THF (125 mL), saturated with oxygen, for 20 h and worked up as in the earlier cases to give a mixture of 300 mg (29%) of 5e, mp 109-110 °C (mixture melting point), 20 mg (2%) of 17a, mp 142-143 °C (mixture melting point), 60 mg (11%) of 13a, mp 42-43 °C (mixture melting point), and 200 mg (21%) of the unchanged starting material (1e), mp 166-167 °C.

II.6.8 Reaction of 3-Phenylsydnone (1f) with Potassium in THF. A solution of 1f (0.8 g, 5 mmol) in THF (125 mL) was shaken with potassium (0.39 g, 10 mmol) for 10 h and worked up as in the earlier cases by treatment with moist THF and removal of the solvent under vacuum to give a residual solid, which was treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 120 mg (14%) of N-nitroso-N-phenylglycine (5f), mp 102-103 °C (mixture melting point), after recrystallization from ethanol. Removal of the solvent from the methylene chloride-extract gave a residue, which was chromatographed over alumina. Elution with petroleum ether gave 10 mg (1%)

of azobenzene (17b), mp 67-68 °C (mixture melting point). Further elution with a mixture (2:3) of benzene and petroleum ether gave 110 mg (24%) of aniline (13b) (superimposable IR spectrum with that of an authentic sample). Subsequent elution with a mixture (7:3) of benzene and petroleum ether gave 190 mg (24%) of the unchanged starting material (1f), mp 133-134 °C (mixture melting point), after recrystallization from ethanol.

In a repeat run, treatment of 1f (0.8 g, 5 mmol) with potassium (0.2 g, 5 mmol) in THF (125 mL) for 10 h, and workup as in the earlier cases gave a mixture of 5f (150 mg, 17%), mp 102-103 °C (mixture melting point), 17b (10 mg, 1%), mp 67-68 °C (mixture melting point), aniline (13b, 80 mg, 17%) (superimposable IR spectrum with that of an authentic sample) and the recovered starting material 1f (300 mg, 38%), mp 133-134 °C (mixture melting point).

II.6.9 Reaction of 3-p-Tolyl-4-phenylsydnone (1a) with Potassium Superoxide. A mixture of 1a (0.5 g, 2 mmol), potassium superoxide (0.29 g, 4 mmol), and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred at room temperature for 24 h, protected from light. The reaction mixture was poured into water (20 mL) and extracted with aqueous sodium chloride. The aqueous layer, on acidification with dilute

hydrochloric acid, gave 100 mg (20%) of phenylglyoxylic acid p-tolylhydrazone (4a) mp 163-164 °C, after recrystallization from a mixture (2:1) of benzene and petroleum ether. Concentration of the mother liquor gave a solid, which on recrystallization from a mixture (1:9) of benzene and petroleum ether gave 40 mg (17%) of benzoic acid (14a), mp 120-121 °C (mixture melting point).

Removal of the solvent from the organic layer under vacuum gave a residue, which was chromatographed over neutral alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave 40 mg (19%) of p-toluidine (13a), mp 42-43 °C (mixture melting point). Further elution with a mixture (2:3) of benzene and petroleum ether gave 20 mg (5%) of N-benzoyl-p-toluidine (15a), mp 157-158 °C (mixture melting point). Subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 140 mg (28%) of the unchanged starting material (1a), mp 151-152 °C (mixture melting point), after recrystallization from ethanol.

II.6.10 Reaction of 3-p-Tolylsydnone (1d) with Potassium Superoxide. A mixture of 1d (0.9 g, 5 mmol), potassium superoxide (0.7 g, 10 mmol), and 18-crown-6 (1.4 g, 5 mmol) in benzene (100 mL) was stirred for 24 h. The reaction mixture was worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. Acidification

of the aqueous layer with dilute hydrochloric acid gave 90 mg (9%) of N-nitroso-N-p-tolylglycine (5d), mp 105-106 °C (mixture melting point), after recrystallization from ethanol. Removal of the solvent from the organic layer gave a solid, which was chromatographed over alumina. Elution with petroleum ether gave 17 mg (2%) of 4,4'-dimethylazobenzene (17a), mp 143-144 °C (mixture melting point), after recrystallization from petroleum ether. Further elution with a mixture (1:9) of benzene and petroleum ether gave 140 mg (26%) of p-toluidine (13a), mp 43-44 °C (mixture melting point), after recrystallization from petroleum ether. Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 170 mg (19%) of the unchanged starting material (1d), mp 144-145 °C (mixture melting point), after recrystallization from ethanol.

II.6.11 Reaction of 3-p-Tolyl-4-methylsydnone (1e) with Potassium Superoxide. A mixture of 1e (0.48 g, 2.5 mmol), potassium superoxide (0.38 g, 5 mmol), and 18-crown-6 (0.68 g, 2.5 mmol) in benzene (100 mL) was stirred at room temperature for 24 h and worked up as in the earlier cases by pouring into water and extracting with aqueous sodium chloride solution. Acidification of the aqueous layer with dilute hydrochloric acid gave 60 mg (11%) of N-nitroso-N-p-tolylalanine (5e), mp 109-110 °C (mixture melting point), after recrystallization from ethanol.

Removal of the solvent from the benzene extract gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 10 mg (2%) of 4,4'-dimethylazobenzene (17a), mp 143-144 °C (mixture melting point), after recrystallization from petroleum ether. Elution with a mixture (1:9) of benzene and petroleum ether gave 55 mg (20%) of p-toluidine (13a), mp 42-43 °C (mixture melting point). Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 175 mg (36%) of the unchanged starting material (1e), mp 166-167 °C (mixture melting point), after recrystallization from ethanol.

II.6.12 Cyclic Voltammetry. Cyclic voltammetric experiments were carried out using Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat, a PAR Model 175 Universal Programmer and a Kipp and Zonen X-Y recorder. Experiments were performed in a standard three compartment cell equipped with a Pt-disc working electrode, Pt-wire counter electrode, and a saturated sodium chloride-calomel electrode (SSCE). Cyclic voltammograms were recorded in acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The direction of the initial scan was cathodic and the scan rate was 100 mV/s.

II.6.13 Pulse Radiolysis. The pulse radiolysis experiments were carried out using a computer controlled apparatus¹⁸ and the irradiation was carried out with 5 ns electron pulse from the Notre Dame 8 MeV ARCO LP-7 linear accelerator using dose rate of $\sim 2 \times 10^{16}$ eV/g per pulse. The solutions (0.2-0.5 mM) was taken in graduated 250 mL cylindrical reservoirs and deaerated by bubbling nitrogen for at least 30 min prior to irradiation. Nitrogen bubbling was continued in the reservoirs from which the solution was allowed to flow gradually and continuously through a quartz cell (1 cm path-length) that was irradiated with electron pulses in a right angle geometry with respect to the analyzing light. Rate constants for the reaction with solvated electrons (e^-_{sol}) were determined from the kinetic analysis of the increased rate of decay of (e^-_{sol}) in presence of the substrate or rate of appearance of the radical anion.

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CHAPTER III

ELECTRON TRANSFER REACTIONS. REACTION OF NITROGEN HETEROCYCLES WITH POTASSIUM

III.1 ABSTRACT

Potassium-induced transformations of a few nitrogen heterocycles such as 2,3-diphenylindole (1a), 2,3-diphenyl-1-methylindole (1b), 1,2,3-triphenylindole (1c), 2,3,4,5-tetraphenylpyrrole (10a), 1,2,3,5-tetraphenylpyrrole (10b), 1-benzyl-2,3,5-triphenylpyrrole (10c), 2,4,5-triphenyloxazole (45a), 4,5-diphenyl-2-methyloxazole (45b), 2,4-diphenyl-5-methyloxazole (45c), and 2,4,5-triphenylimidazole (50) have been examined with a view to studying the nature of the products formed in these reactions and also to understand the reaction pathways. The reaction of 1a with potassium in THF, for example, gave 9H-dibenzo[a,c]carbazole (8a), whereas 1c, under analogous conditions, gave a mixture of 9-phenyl-9H-dibenzo[a,c]carbazole (8c) and 2,3-diphenylindole (1a). On the otherhand, treatment of 1b with potassium in THF gave 1a, as the only isolable product. In contrast, when the reactions of 1a,c were carried out with potassium in THF, saturated with oxygen and with potassium superoxide in benzene containing 18-crown-6, a mixture of 2-benzamidobenzophenone (9a), the carbazoles 8a,c, and 2,3-diphenylindole

(1a) was formed, in each case. The reaction of 10a with potassium in THF did not give any isolable product; most of the starting material could be recovered unchanged. On the other-hand, treatment of 10a, with potassium in THF, saturated with oxygen gave a mixture of products consisting of the lactam 17a, the benzoylaminostilbene 22a, tetraphenylpyrazine (33), benzamide (24a), and benzoic acid (23). Similar results were obtained when the reaction of 10a was carried out with potassium superoxide. The reaction of N-substituted pyrroles such as 10b,c with potassium gave the N-unsubstituted pyrrole 13b in each case, along with some unchanged starting material. However, when the reactions of 10b,c were carried out with potassium in THF, saturated with oxygen, a mixture of 13b, the lactam 17b, the butanone 43b, the 1,4-dione 44b, the amides 24a-c, and benzoic acid (23) was obtained in each case. On the other hand, attempted reactions of 10b,c with potassium superoxide did not give any isolable product; most of the starting material could be recovered unchanged in each case. Treatment of the -oxazole 45a with potassium gave a mixture of N-(1,2-diphenylethyl)-benzamide (48a) and benzoic acid (23), whereas 45b,c, under analogous conditions, gave the N-vinylamides 49b,c and benzoic acid (23). In contrast, the reaction of the imidazole 50, with potassium in THF did not give any isolable product; most of 50 was recovered unchanged. However, when the reaction of 50 was carried out with

potassium in THF, saturated with oxygen, and with potassium superoxide, dibenzamide (21a) was isolated in each case.

Reasonable mechanisms involving radical anion and dianion intermediates and their subsequent transformations have been suggested to explain the formation of the various products. Cyclic voltammetric studies have been carried out to measure the reduction potentials of these radical anion and dianion intermediates. The radical anions of these substrates have also been generated pulse radiolytically in methanol and their absorption spectra were recorded.

III.2 INTRODUCTION

Only very few examples of the reaction of nitrogen heterocycles with alkali metals are reported in the literature¹⁻⁵. It has been reported that pyrrole is not reducible by potassium in liquid ammonia, whereas indoles are reduced to the corresponding dihydroindoles on treatment with sodium in ammonia.² However, when indole is reduced by a large excess of lithium and methanol, a mixture of 4,7-dihydroindole and 4,5,6,7-tetrahydroindole is reported to be formed in equal amounts.³ Subsequent studies by Remers et al.⁴ have shown that ring selectivity in the reduction of indoles and quinolines by sodium in liquid ammonia could be controlled, depending on whether the reduction is carried out in the presence of methanol or not. The sodium-

ethanol reduction of 2,4,5-triphenyloxazole has been reported to give N-(2-oxy-1,2-diphenylethyl)-benzylamine, whereas, the reduction of 4,5-diphenyl-2-methyloxazole gives N-(1,2-diphenylethyl)-acetamide.⁵

The objective of the present investigation has been to examine the reactions of some selected heterocyclic substrates such as indoles, pyrroles, oxazoles, and imidazole with potassium in THF, with a view to understanding the nature of the products formed in these reactions and also their reaction pathways.

III.3 RESULTS AND DISCUSSION

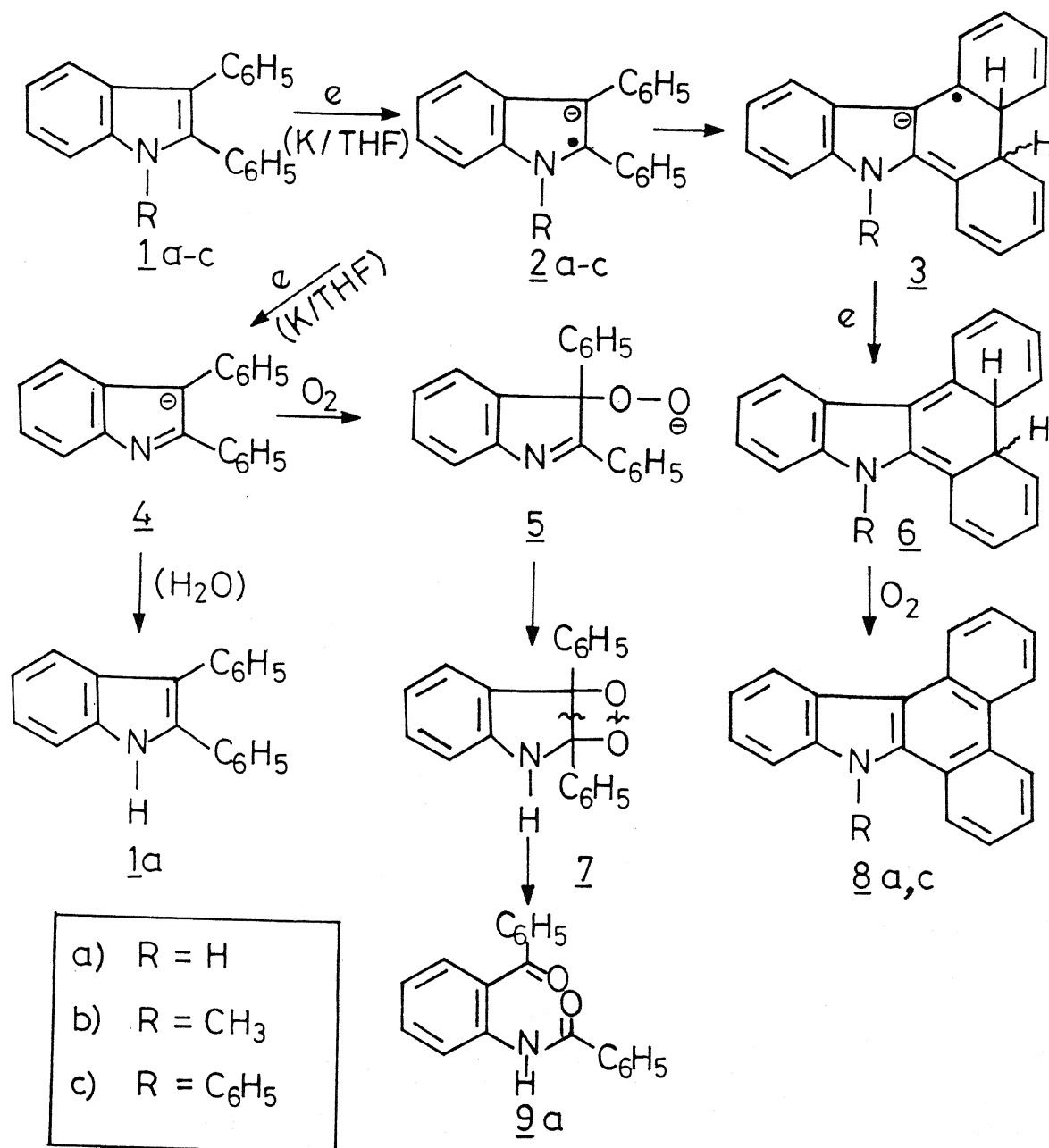
In the present studies, we have examined the reactions of 2,3-diphenylindole (1a), 2,3-diphenyl-1-methylindole (1b), 1,2,3-triphenylindole (1c), 2,3,4,5-tetraphenylpyrrole (10a), 1,2,3,5-tetraphenylpyrrole (10b), and 1-benzyl-2,3,5-triphenylpyrrole (10c) with potassium in THF. In addition, the reactions of a few oxazoles such as 2,4,5-triphenyloxazole (45a), 4,5-diphenyl-2-methyloxazole (45b), and 2,4-diphenyl-5-methyloxazole (45c) and an imidazole such as 2,4,5-triphenylimidazole (50) with potassium have been examined. The reaction of 1a with potassium in THF, for example, gave 9H-dibenzo[a,c]carbazole (8a, 49%), whereas 1c, under analogous conditions, gave a mixture of 9-phenyl-9H-dibenzo[a,c]carbazole (8c, 20%) and 2,3-diphenylindole (1a, 19%). The reaction of 1b, with potassium gave 1a (68%), as

the only isolable product. In contrast, the reactions of 1a,c with potassium in THF, saturated with oxygen, and with potassium superoxide gave a mixture of 2-benzamidobenzophenone (9a, 20-34%), the carbazoles 8a,c (10-13%), and 2,3-diphenylindole (1a, 7-9%), in each case.

The formation of the different products in the reaction of 1a-c with potassium in THF can be understood in terms of the reaction pathways shown in Scheme III.1. It has been assumed that the indoles 1a-c, initially accept an electron to form the corresponding radical anion intermediates 2a-c, which could undergo radical cyclization to give the intermediate 3, and ultimately the carbazoles 8a,c, on workup. The radical anion intermediates 2a-c could also undergo further reduction to give the anionic intermediate 4, which could either give the unsubstituted indole 1a, on protonation, or undergo further reaction with oxygen, under the conditions of workup, to give the oxygenated product 9a, as shown in Scheme III.1.

An attempted reaction of a pyrrole such as 2,3,4,5-tetraphenylpyrrole (10a) with potassium in THF did not give any product; most of the starting material could be recovered unchanged. However, when the reaction of 10a was carried out with potassium in THF, saturated with oxygen, a mixture of α -benzoylamino- α' -benzoylstilbene (22a), tetraphenylpyrazine (33, 13%),

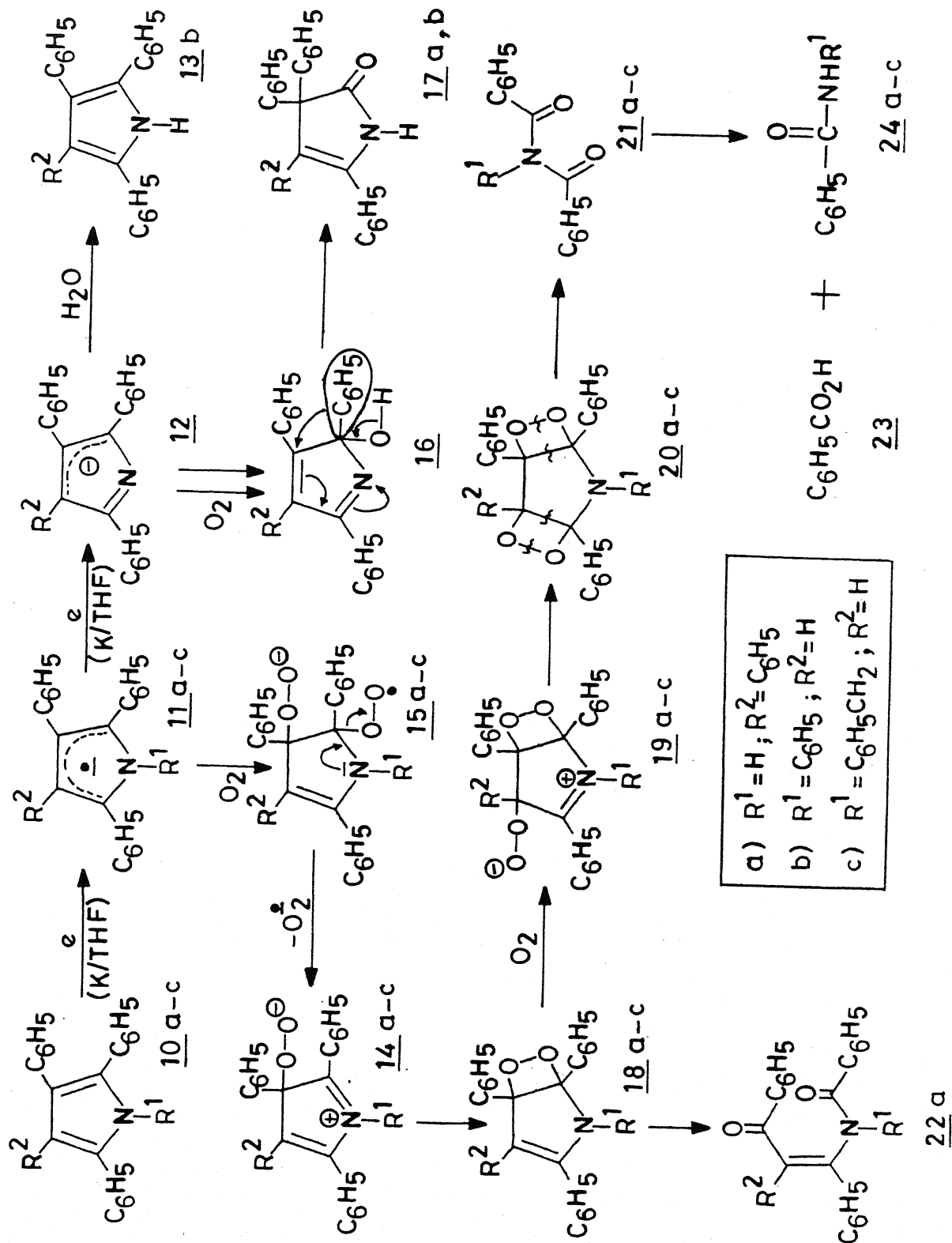
Scheme III.1



15%), benzoic acid (23, 10%), and some unchanged starting material (10a, 30%) was obtained. The reactions of the N-substituted pyrroles 10b,c with potassium gave the N-unsubstituted pyrrole 13b (30-33%), in each case, whereas, the reactions of 10b,c with potassium in THF, saturated with oxygen gave a mixture of 13b (7-8%), 2,4,4-triphenyl-2-pyrrolin-5-one (17b, 10-12%), benzoic acid (23, 14-15%), the amides 24a-c (9-17%), 1,3,4-triphenylbutan-1-one (43b, 12-14%), and 1,2,4-triphenylbutan-1,4-dione (44b, 11-13%), in each case.

The formation of the different products in the reaction of 10a-c with potassium in THF could be rationalized in terms of the reaction pathways shown in Schemes III.2-III.4. It is assumed that the initial step in the reaction involves the formation of the radical anion intermediates 11a-c, which can combine with oxygen under the conditions of work up to give the oxygenated products such as 22a, 23, and 24a-c, as shown in Scheme III.2. The radical anion intermediates 11a-c could also undergo further reduction to give the anionic species 12a,b, which on protonation could give the pyrroles 10a and 13b or undergo further oxygenation, under the conditions of workup, to give ultimately 17a,b, as shown in Scheme III.2. The formation of tetraphenylpyrazine (33) in the reaction of 10a with potassium, however, could be rationalized in terms of the

Scheme III.2



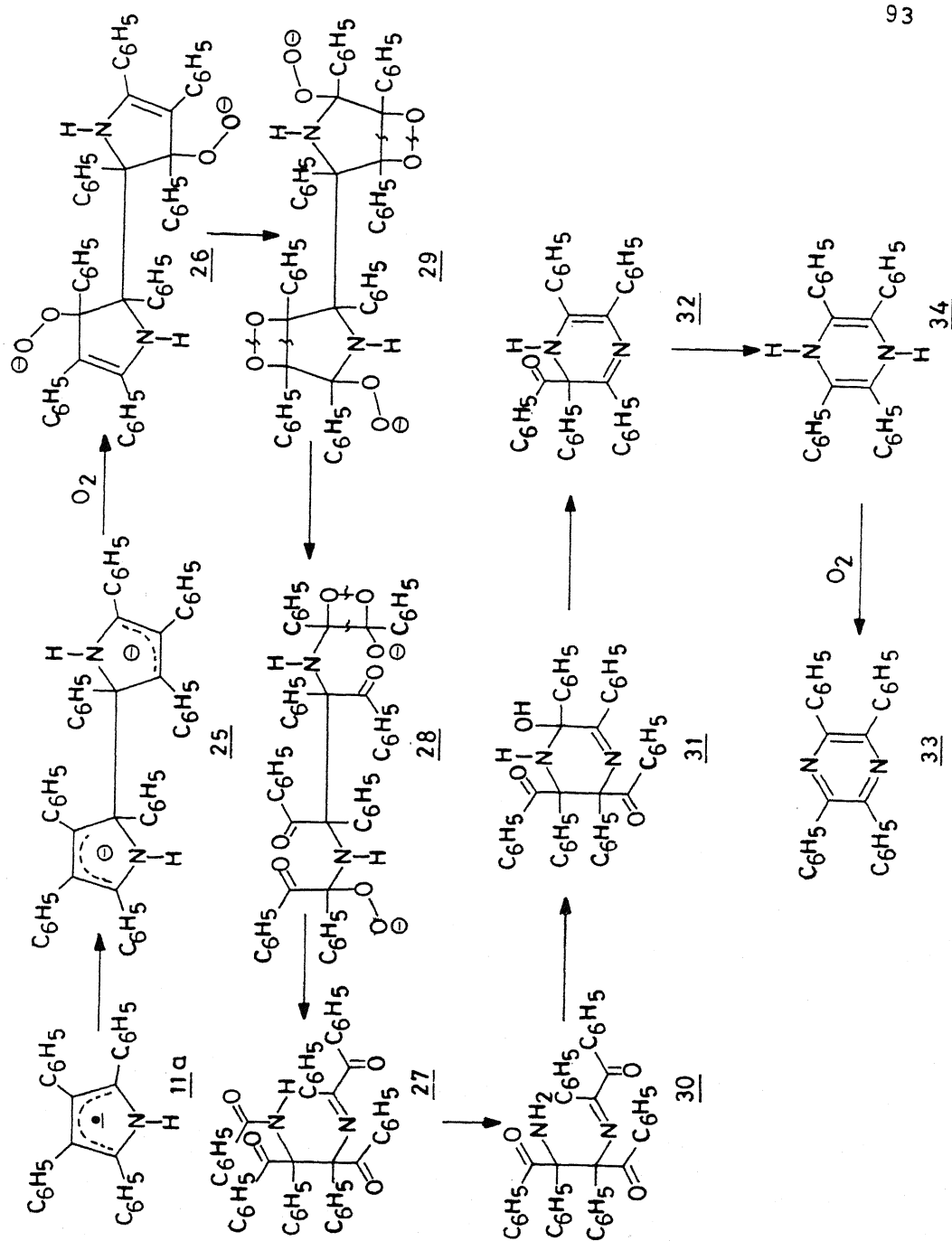
pathways shown in Scheme III.3. The initially formed radical anion intermediate 11a, can undergo dimerization to give the dianionic species 25, which can react with oxygen under the conditions of workup to give ultimately 33, as shown in Scheme III.3.

The formation of products such as 43b and 44b in the reactions of 10b,c with potassium, can be rationalized in terms of the pathways shown in Scheme III.4. The initially formed radical anion intermediates 11a-c, can undergo further reduction to give the dianion intermediate 38, which can ultimately lead to 43b. The radical anions 11a-c can also combine with oxygen to give the hydroperoxy intermediate 35, which will ultimately lead to 44b, as shown in Scheme III.4.

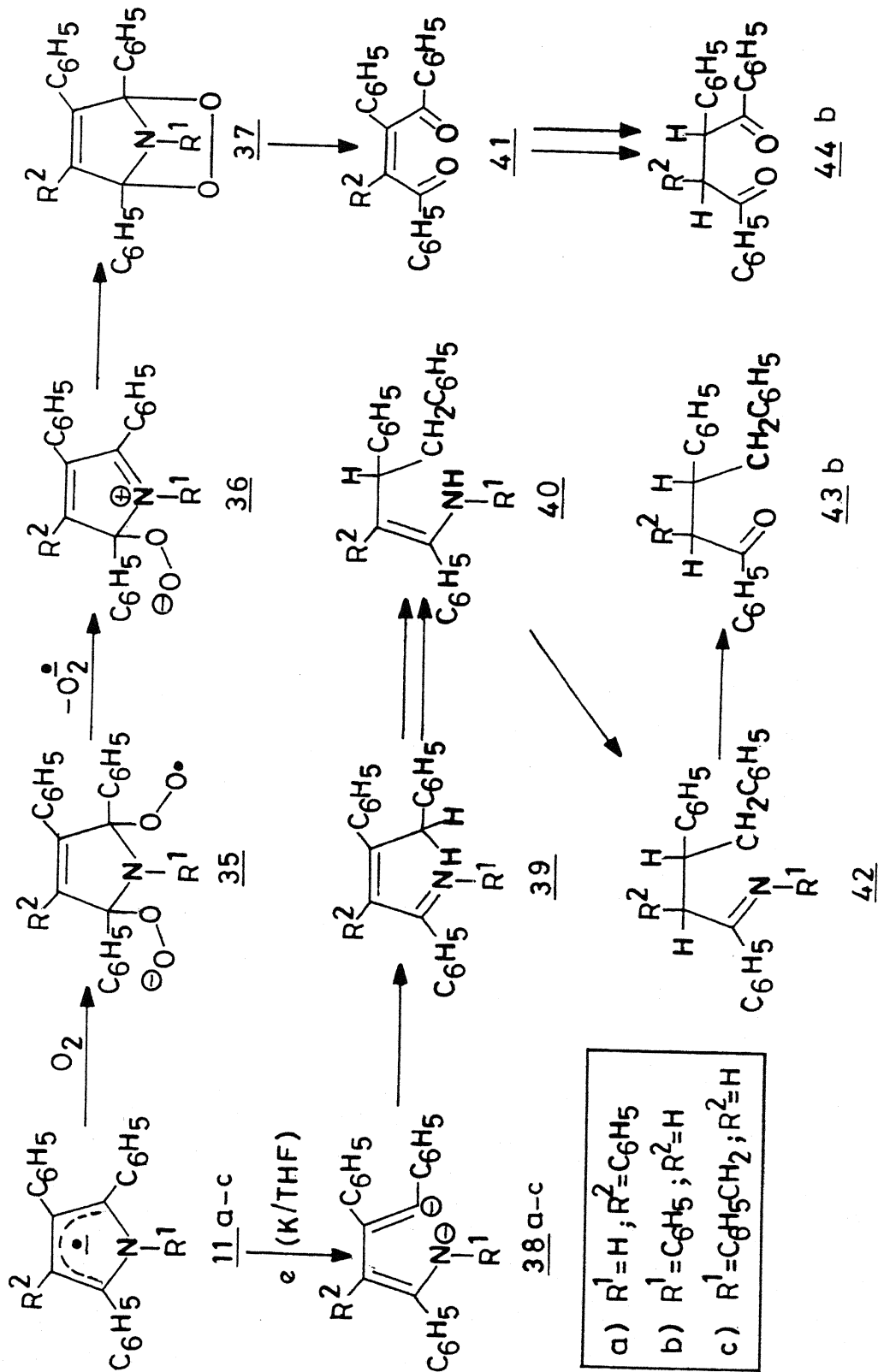
The reaction of an oxazole such as 2,4,5-triphenyloxazole (45a) with potassium in THF gave a mixture of N-(1,2-diphenylethyl)-benzamide (48a, 27%) and benzoic acid (23, 5%), whereas the oxazoles 45b,c, under analogous conditions gave a mixture of the N-vinylamides 49b,c (30-37%) and benzoic acid (23, 4%). In contrast, the reaction of the imidazole 50, under similar conditions did not give any product; however, treatment of 50 with potassium in THF, saturated with oxygen, gave dibenzamide (21a, 21%) as the only isolable product.

The formation of products such as 48a, 49b,c, and 50 in the reaction of 45a-c and 50 with potassium may be rationalized

Scheme III.3



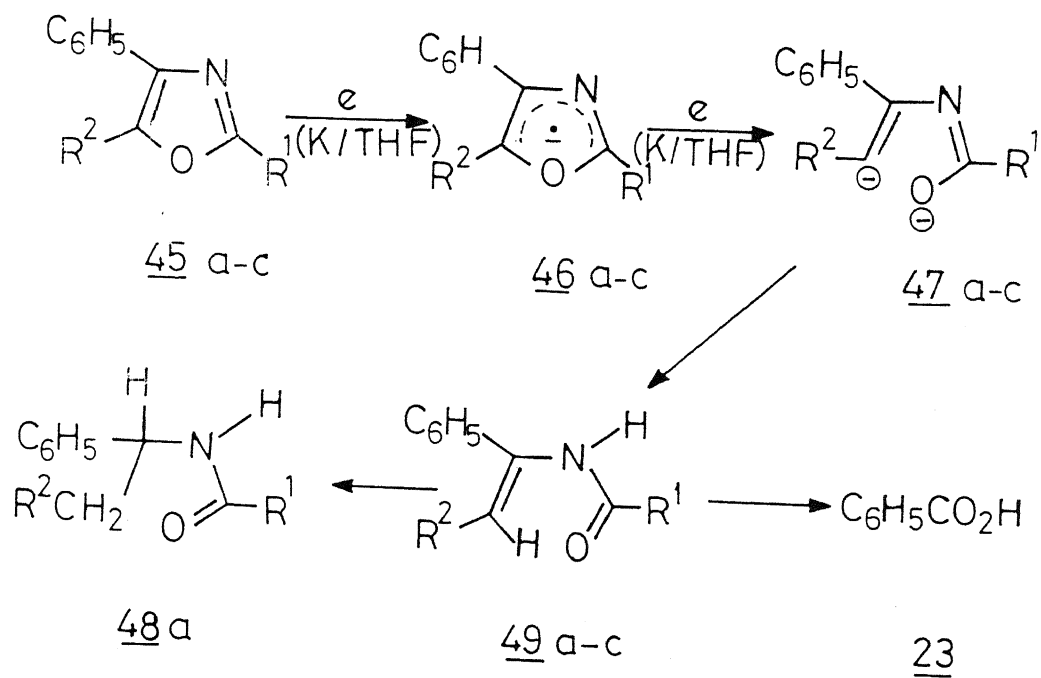
Scheme III.4



in terms of the pathways shown in Schemes III.5 and III.6. The initially formed radical anion intermediates 46a-c, for example, could undergo further reduction, to the dianion intermediates 47a-c, which can subsequently be transformed to products such as 48a, 49b,c, and 23, as shown in Scheme III.5. The formation of dibenzamide (21a) from 50, likewise, can be rationalized in terms of the further transformations of the radical anion intermediate 51, as shown in Scheme III.6.

To examine whether any of the oxygenated products formed in the reaction of 1a-c, 10a-c, 45a-c, and 50 with potassium in THF arises through the involvement of superoxide in these reactions, we have carried out the reaction of these substrates with potassium superoxide in benzene containing 18-crown-6. It is interesting to note that the products formed in most of these cases closely resembled to those formed in the reaction of these substrates with potassium in THF, saturated with oxygen. In the case of the N-substituted pyrroles 10b,c, however, the reaction with potassium superoxide did not give any product and it is likely that in these cases, the radical anion intermediates 11b,c are not formed through electron transfer from potassium superoxide. The fact that oxygenated products were observed in the case of 10a, on the otherhand, would suggest that potassium superoxide may be abstracting the NH proton from 10a to give the corresponding anionic species initially, which may

Scheme III.5

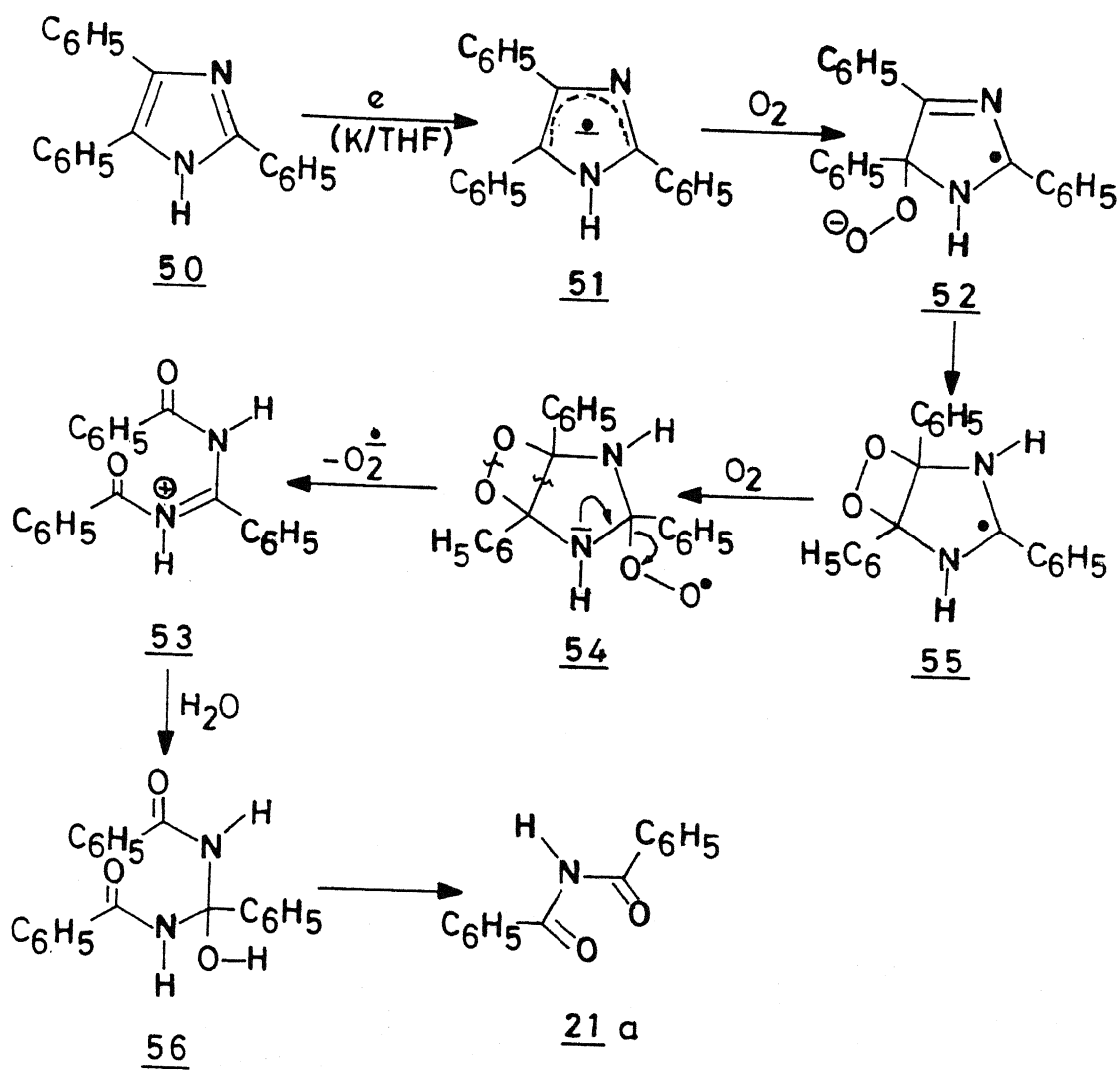


- a) $\text{R}^1 = \text{R}^2 = \text{C}_6\text{H}_5$

b) $\text{R}^1 = \text{CH}_3, \text{R}^2 = \text{C}_6\text{H}_5$

c) $\text{R}^1 = \text{C}_6\text{H}_5, \text{R}^2 = \text{CH}_3$

Scheme III.6



then undergo further transformations to give the observed products.

The structures of all the products formed in the reaction of 1a-c, 10a-c, 45a-c, and 50 with potassium were established on the basis of analytical results, spectral data and comparison with authentic samples, wherever possible.

III.4 CYCLIC VOLTAMMETRIC STUDIES⁶

In the present study, we have generated electrochemically, the radical anions of 1a-c, 10a-c, 45a-c, and 50, the substrates under investigation. The cyclic voltammograms of 1a-c, 10a-c, 45a-c, and 50 are shown in Figure III.1 and the reduction potentials are summarized in Table III.1. The substrates 1a-c, 10a-c, and 50 exhibited irreversible reduction peaks with the reduction potentials in the region of -1.88 to -2.6 V versus SSCE, whereas, substrates 45a-c underwent reversible reduction with half peak potentials in the range of -2.21 to -2.46 V versus SSCE.

III.5 PULSE RADIOLYSIS STUDIES⁷

In the present investigation, the radical anions of 1a-c, 10a-c, 45a-c, and 50 were generated in methanol pulse radiolytically and their absorption spectra are presented in Figure III.2. These radical anions showed strong absorption maxima

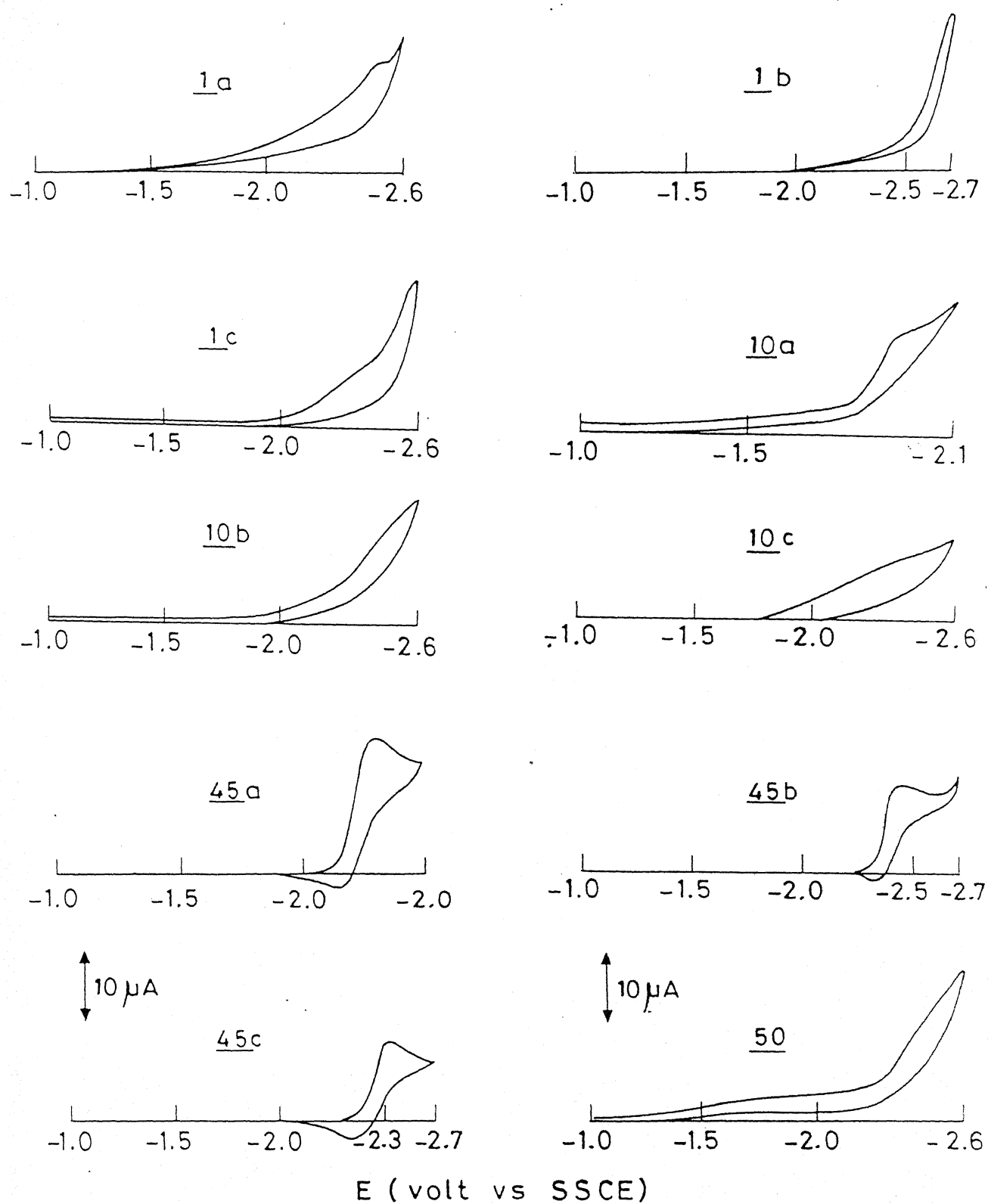


Figure III.1 Cyclic voltammograms of 1a-c, 10a-c, 45a-c and 50

Table III.1 Electrochemical, spectral and kinetic data of indoles (1a-c), pyrroles (10a-c), oxazoles (45a-c) and imidazole (50)

| Substrate | Reduction Potential ^a E _{p/2} (V vs SSCE) | Absorption Maxima ^c of Radical anion (nm) | k ^{c,d} 10 ⁹ M ⁻¹ S ⁻¹ | $\frac{c,e}{\tau_{1/2}}$ μ s |
|------------|--|--|---|-------------------------------------|
| <u>1a</u> | -2.35 | 365 | 3.3 | 8 |
| <u>1b</u> | -2.6 | 365 | 5.4 | 275 |
| <u>1c</u> | -2.25 | 367 (~460) | 5.1 | 9 |
| <u>10a</u> | -1.88 | 370 (440) | 6.7 | 12 |
| <u>10b</u> | -2.35 | 365 (440) | 7.8 | 19 |
| <u>10c</u> | -2.10 | 346, 365, (450) | 4.7 | 33 |
| <u>45a</u> | -2.21 (-2.23) ^b | 345, 380 | 14.9 | 4 |
| <u>45b</u> | -2.36 (-2.38) ^b | 330, (~550) | 10.6 | 10 |
| <u>45c</u> | -2.46 (-2.49) ^b | 350 | 10.8 | 2 |
| <u>50</u> | -2.42 | 375 | 5.1 | 2 |

a) In acetonitrile containing 0.1 M tetrabutylammonium perchlorate. b) The values in parentheses are the standard reduction potentials as obtained from the reversible cyclic voltammograms.
c) In methanol. d) Rate constant for the reaction of the substrate with solvated electron (e⁻sol) in methanol. e) Half-life of the radical anion in methanol.

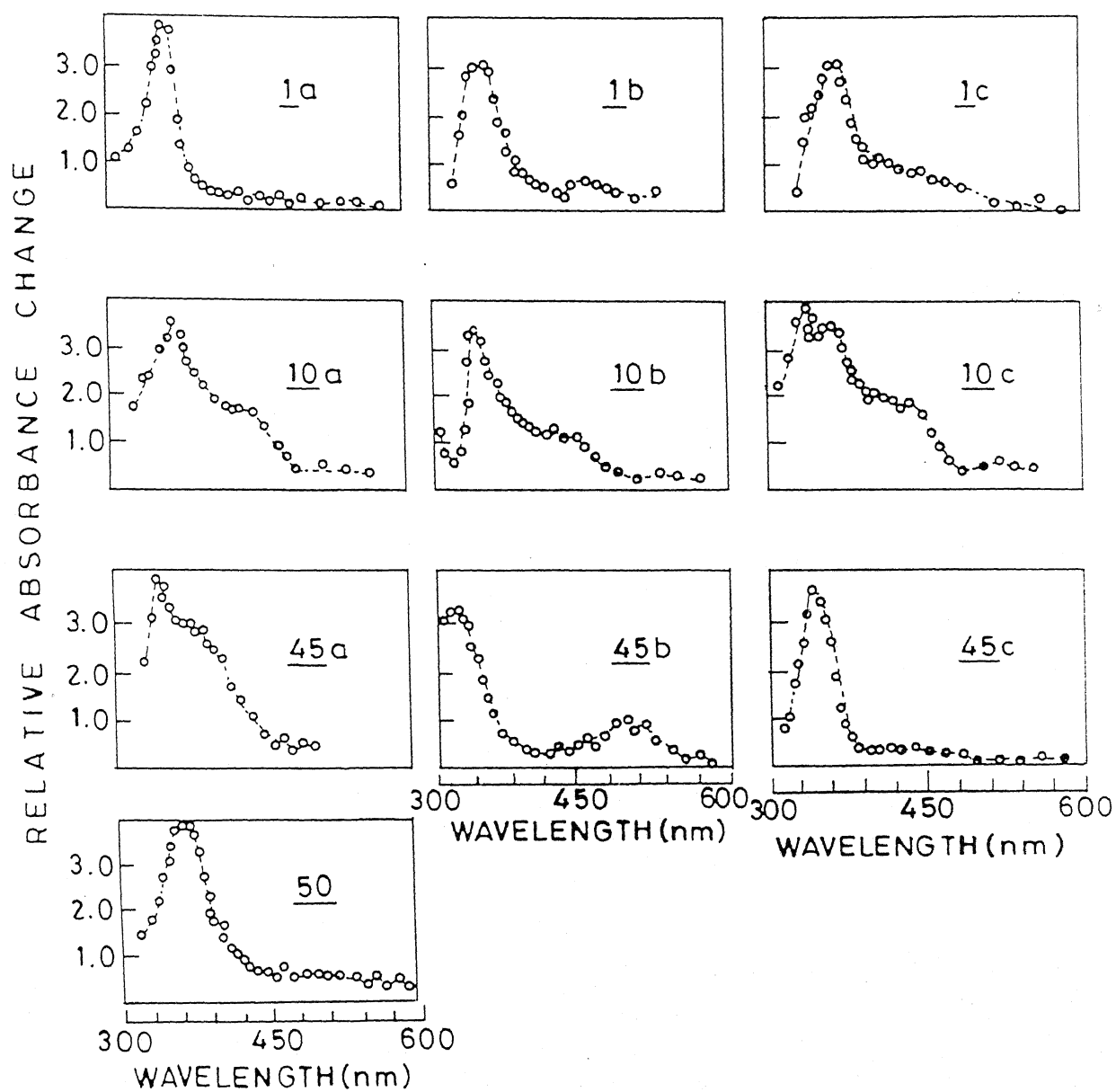


Figure III.2 Absorption spectra of the pulse radiolytically generated radical anions from 1a-c, 10a-c, 45a-c and 50

in the region of 330-500 nm and had a half-life of 2-275 μ s in methanol. It is evident from table III.1 that these radical anions are formed from their appropriate precursors through the reaction with solvated electrons under diffusion controlled rates.

III.6 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The petroleum ether used was the fraction with bp 60-80 $^{\circ}$ C. THF used was dried over sodium and was distilled before use. Gold Label (Aldrich) acetonitrile was used for cyclic voltammetric studies and spectral grade methanol (Fischer Scientific) was used for pulse radiolysis.

III.6.1 Starting Materials. 2,3-Diphenylindole (1a),⁸ mp 123-124 $^{\circ}$ C, 2,3-diphenyl-1-methylindole (1b),⁸ mp 129-130 $^{\circ}$ C, 1,2,3-triphenylindole (1c),⁹ mp 186-187 $^{\circ}$ C, 2,3,4,5-tetraphenylpyrrole (10a),¹⁰ mp 212-213 $^{\circ}$ C, 1,2,3,5-tetraphenylpyrrole (10b),¹¹ mp 199-200 $^{\circ}$ C, 1-benzyl-2,3,5-triphenylpyrrole (10c),¹¹ mp 166-167 $^{\circ}$ C, 2,4,5-triphenyloxazole (45a),¹² mp 116-117 $^{\circ}$ C, 4,5-diphenyl-2-methyloxazole (45b),¹² bp 210-212 $^{\circ}$ C (18 mm), 2,4-diphenyl-5-methyloxazole (45c),¹³ mp 74-75 $^{\circ}$ C, and 2,4,5-triphenylimidazole (50),^{12,14} mp 274-275 $^{\circ}$ C were prepared by reported procedures.

III.6.2 Reaction of 2,3-Diphenylindole (1a) with Potassium in THF. A solution of 1a (0.81 g, 3 mmol) in THF (125 mL) was shaken with potassium (0.23 g, 6 mmol) for 8 h in a Schlenk tube. On completion of the reaction, the mixture was treated with moist THF and the solvent was removed under vacuum to give a residual solid, which was treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 240 mg (30%) of the unchanged starting material (1a), mp 123-124 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Further elution with petroleum ether gave 390 mg (49%) of 9H-dibenzo[a,c]carbazole (8a), mp 192-193 °C (mixture melting point),¹⁵ after recrystallization from a mixture (1:9) of benzene and petroleum ether.

In a repeat run, a solution of 1a (0.81 g, 3 mmol) in THF (125 mL), saturated with oxygen, was shaken with potassium (0.23 g, 6 mmol) for 7 h and worked up by treatment with moist THF and removal of the solvent under reduced pressure to give a solid material, which was subsequently treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a residue, which was

chromatographed over neutral alumina. Elution with petroleum ether gave 490 mg (60%) of the unchanged starting material (1a), mp 123-124 °C (mixture melting point). Further elution with petroleum ether gave 80 mg (10%) of 8a, mp 192-193 °C, (mixture melting point). Subsequent elution with a mixture (4:1) of benzene and petroleum ether gave 180 mg (20%) of 2-benzamido-benzophenone (9a), mp 89-90 °C (mixture melting point).¹⁵

III.6.3 Reaction of 2,3-Diphenyl-1-methylindole (1b) with Potassium in THF. Treatment of 1b (0.57 g, 2 mmol) with potassium (0.16 g, 4 mmol) in THF (125 mL) for 15 h and workup as in the earlier cases by treatment with moist THF and removal of the solvent under vacuum gave a residual solid, which was subsequently treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a residue, which was chromatographed over neutral alumina. Elution with petroleum ether gave 110 mg (19%) of the unchanged starting material (1b), mp 129-130 °C (mixture melting point). Further elution with petroleum ether gave 370 mg (68%) of 2,3-diphenylindole (1a), mp 123-124 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

In a repeat run, 1b (0.57 g, 2 mmol) was treated with potassium (0.16 g, 4 mmol) in THF (125 mL), saturated with

oxygen, for 4 h and worked up as in the earlier case to give a mixture of 40 mg (7%) of 1a, mp 123-124 °C (mixture melting point) and 470 mg (83%) of the unchanged starting material (1b), mp 129-130 °C (mixture melting point).

III.6.4 Reaction of 1,2,3-Triphenylindole (1c) with Potassium in THF. A solution of 1c (1 g, 3 mmol) in THF (125 mL) was treated with potassium (0.23 g, 6 mmol) for 15 h and worked up as in the earlier cases to give a residual solid, which was treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a product mixture which was chromatographed over neutral alumina. Elution with petroleum ether gave 380 mg (38%) of the unchanged starting material (1c), mp 186-187 °C (mixture melting point). Further elution with petroleum ether gave 150 mg (19%) of 2,3-diphenylindole (1a), mp 123-124 °C (mixture melting point). Subsequent elution with petroleum ether gave 200 mg (20%) of 9-phenyl-9H-dibenzo-[a,c]carbazole (8c), mp 197-198 °C (mixture melting point),¹⁵ after recrystallization from a mixture (1:9) of benzene and petroleum ether.

In a repeat run, 1c (1 g, 3 mmol) was treated with potassium (0.23 g, 6 mmol) in THF (125 mL), saturated with oxygen for 7 h and worked up as in the earlier cases to give

a mixture of 80 mg (8%) of 8c, mp 197-198 °C, 70 mg (9%) of 1a, mp 123-124 °C (mixture melting point), 250 mg (29%) of 9a, mp 89-90 °C, and 270 mg (27%) of the unchanged starting material (1c), mp 186-187 °C (mixture melting point).

III.6.5 Reaction of 2,3,4,5-Tetraphenylpyrrole (10a) with Potassium in THF. Treatment of 10a (1.1 g, 3 mmol) with potassium (0.23 g, 6 mmol) in THF (125 mL) for 10 h and workup of the reaction mixture in the usual manner gave 640 mg (59%) of the unchanged starting material (10a), mp 212-213 °C (mixture melting point).

In a repeat experiment, 10a (1.1 g, 3 mmol) was treated with potassium (0.23 g, 6 mmol) in THF (125 mL), saturated with oxygen for 6 h and worked up in the usual manner to give a residual solid, which was treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 36 mg (10%) of benzoic acid (23), mp 120-121 °C (mixture melting point). Removal of the solvent from the methylene chloride-extract gave a residual solid, which was chromatographed over neutral alumina. Elution with petroleum ether gave 330 mg (30%) of the unchanged starting material (10a), mp 212-213 °C. Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 150 mg (13%) of tetraphenylpyrazine (33), mp 249-250 °C (mixture melting point), after recrystallization from ethanol. Further elution

with a mixture (2:3) of benzene and petroleum ether gave 80 mg (7%) of α -benzoylamino- α' -benzoylstilbene (22a), mp 190-191 °C (mixture melting point),¹⁶ after recrystallization from ethanol. Subsequent elution with a mixture (2:3) of benzene and petroleum ether gave 220 mg (19%) of 2,3,4,4-tetraphenyl-2-pyrrolin-5-one (17a), mp 213-214 °C (mixture melting point),^{17,18} after recrystallization from ethanol. Continued elution with a mixture (1:1) of benzene and petroleum ether gave 53 mg (15%) of benzamide (24a), mp 128-129 °C (mixture melting point), after recrystallization from hot water.

III.6.6 Reaction of 1,2,3,5-Tetraphenylpyrrole (10b) with Potassium in THF. A mixture of 10b (1.1 g, 3 mmol) and potassium (0.23 g, 6 mmol) in THF (125 mL) was shaken for 10 h and worked up in the usual manner to give a residual solid, which was treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a solid material, which was chromatographed over neutral alumina. Elution with petroleum ether gave 540 mg (49%) of the unchanged starting material (10b), mp 199-200 °C (mixture melting point). Further elution with petroleum ether gave 260 mg (30%) of 2,3,5-triphenylpyrrole (13b), mp 140-141 °C (mixture melting point).¹¹

In a repeat run, treatment of 10b (1.1 g, 3 mmol) with potassium (0.23 g, 6 mmol) in THF (125 mL), saturated with

oxygen, for 10 h and workup in the usual manner gave a residual solid, which was treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 50 mg (14%) of benzoic acid (23), mp 120-121 °C (mixture melting point).

Removal of the solvent from the organic layer gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 99 mg (9%) of the unchanged starting material (10b), mp 199-200 °C (mixture melting point). Further elution with petroleum ether gave 60 mg (7%) of 2,3,5-triphenylpyrrole (13b), mp 140-141 °C (mixture melting point). Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 88 mg (12%) of 1,3,4-triphenylbutan-1-one (43b), mp 112-113 °C (mixture melting point),¹⁹ after recrystallization from ethanol. Continued elution with a mixture (2:3) of benzene and petroleum ether gave 85 mg (16%) of benzanilide (24b), mp 163-164 °C (mixture melting point), after recrystallization from ethanol. Elution with a mixture (1:1) of benzene and petroleum ether gave 30 mg (9%) of benzamide (24a), mp 128-129 °C (mixture melting point), after recrystallization from hot water. Subsequent elution with a mixture (3:2) of benzene and petroleum ether gave 120 mg (13%) of 1,2,4-triphenylbutan-1,4-dione (44b), mp 125-126 °C (mixture melting point).¹¹

Further elution with a mixture (4:1) of benzene and petroleum ether gave 90 mg (10%) of 2,4,4-triphenyl-2-pyrrolin-5-one (17b), mp 224-225 °C (mixture melting point),²⁰ after recrystallization from ethanol.

III.6.7 Reaction of 1-Benzyl-2,3,5-triphenylpyrrole (10c) with Potassium in THF. A mixture of 10c (1.2 g, 3 mmol) and potassium (0.23 g, 6 mmol) in THF (125 mL) was shaken for 10 h. Workup as in the earlier cases gave a residual solid, which was chromatographed over neutral alumina. Elution with petroleum ether gave 540 mg (45%) of the unchanged starting material (10c), mp 166-167 °C (mixture melting point). Subsequent elution with petroleum ether gave 300 mg (33%) of 2,3,5-triphenylpyrrole (13b), mp 140-141 °C (mixture melting point), after recrystallization from ethanol.

In a repeat run, 10c (1.2 g, 3 mmol) was treated with potassium (0.23 g, 6 mmol) in THF (125 mL), saturated with oxygen, for 10 h and worked up as in the earlier cases. Acidification of the aqueous fraction with dilute hydrochloric acid gave 57 mg (15%) of benzoic acid (23), mp 120-121 °C (mixture melting point). Removal of the solvent from the organic layer gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 165 mg

(14%) of the unchanged starting material (10c), mp 166-167 °C (mixture melting point). Further elution with petroleum ether gave 72 mg (8%) of 2,3,5-triphenylpyrrole (13b), mp 140-141 °C (mixture melting point). Continued elution with a mixture (1:4) of benzene and petroleum ether gave 130 mg (14%) of 1,3,4-triphenylbutan-1-one (43b), mp 112-113 °C (mixture melting point). Elution with a mixture (2:3) of benzene and petroleum ether gave 110 mg (17%) of N-benzylbenzamide (24c), mp 105-106 °C (mixture melting point). Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 33 mg (9%) of benzamide (24a), mp 128-129 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 106 mg (11%) of 1,2,4-triphenylbutan-1,4-dione (44b), mp 125-126 °C (mixture melting point). Finally, elution with a mixture (4:1) of benzene and petroleum ether gave 115 mg (12%) of 2,4,4-triphenyl-2-pyrrolin-5-one (17b), mp 224-225 °C (mixture melting point).

III.6.8 Reaction of 2,4,5-Triphenyloxazole (45a) with Potassium in THF. A mixture of 45a (0.6 g, 2 mmol) and potassium (0.16 g, 4 mmol) in THF (125 mL) was shaken for 10 h and worked up as in the earlier cases to give a residual solid, which was subsequently treated with water and extracted with methylene chloride. Acidification of the aqueous layer

with dilute hydrochloric acid gave 10 mg (5%) of benzoic acid (23), mp 120-121 °C (mixture melting point). Removal of the solvent from the methylene chloride-extract gave a residual mass, which was chromatographed over neutral alumina. Elution with petroleum ether gave 280 mg (47%) of the unchanged starting material (45a), mp 116-117 °C (mixture melting point). Further elution with petroleum ether gave 160 mg (27%) of N-(1,2-diphenylethyl)-benzamide (48a), mp 177-178 °C (mixture melting point),²¹ after recrystallization from ethanol.

In a repeat run, 45a (0.6 g, 2 mmol) was treated with potassium (0.16 g, 4 mmol) in THF (125 mL), saturated with oxygen, for 20 h and worked up as in the earlier case to give a mixture of 400 mg (29%) of 45a, mp 116-117 °C (mixture melting point), 90 mg (15%) of 48a, mp 177-178 °C (mixture melting point), and 20 mg (10%) of benzoic acid (23), mp 120-121 °C (mixture melting point).

III.6.9 Reaction of 4,5-Diphenyl-2-methyloxazole (45b) with Potassium in THF. Treatment of 45b (0.47 g, 2 mmol) with potassium (0.16 g, 4 mmol) in THF (125 mL) for 10 h and workup as in the earlier cases gave a residual solid, which was treated with water and extracted with methylene chloride. Acidification of the aqueous fraction with dilute hydrochloric acid gave 10 mg (4%) of benzoic acid (23), mp 120-121 °C (mixture melting point).

Removal of the solvent from the methylene chloride-extract gave a solid, which was chromatographed over neutral alumina. Elution with petroleum ether gave 230 mg (45%) of the unchanged starting material (45b), bp 210-212 °C (18 mm). Further elution with petroleum ether gave 190 mg (37%) of N-(1,2-diphenylethyl)-acetamide (49b), mp 175-176 °C (mixture melting point).²²

In a repeat run, treatment of 45b (0.47 g, 2 mmol) with potassium (0.16 g, 4 mmol) in THF (125 mL), saturated with oxygen for 10 h and workup as in the earlier case gave a mixture of 70 mg (14%) of 49b, mp 175-176 °C (mixture melting point), 300 mg (59%) of the unchanged starting material (45b), bp 210-212 °C (18 mm), and 30 mg (11%) of benzoic acid (23), mp 120-121 °C (mixture melting point).

III.6.10 Reaction of 2,4-Diphenyl-5-methyloxazole (45c) with Potassium in THF. Treatment of 45c (0.47 g, 2 mmol) with potassium (0.16 g, 4 mmol) in THF (125 mL) for 10 h and workup as in the earlier cases gave a residual solid, which was treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 10 mg (4%) of benzoic acid (23), mp 120-121 °C (mixture melting point).

Removal of the solvent under vacuum from the methylene

chloride-extract gave a residual solid, which was chromatographed over neutral alumina. Elution with petroleum ether gave 260 mg (52%) of the unchanged starting material (45c), mp 74-75 °C (mixture melting point). Further elution with petroleum ether gave 150 mg (30%) of N-(1-phenyl-1-propenyl)-benzamide (49c), mp 164-165 °C (mixture melting point),²³ after recrystallization from ethanol.

In a repeat run, 45c (0.47 g, 2 mmol) was treated with potassium (0.16 g, 4 mmol) in THF (125 mL), saturated with oxygen, for 10 h and worked up as in the earlier cases to give a mixture of 80 mg (16%) of 49c, mp 164-165 °C (mixture melting point), 20 mg (9%) of 23, mp 120-121 °C (mixture melting point), and 310 mg (62%) of the unchanged starting material (45c), mp 74-75 °C (mixture melting point).

III.6.11 Reaction of 2,4,5-Triphenylimidazole (50)
with Potassium in THF. A solution of 50 (0.6 g, 2 mmol) in THF (125 mL) was shaken with potassium (0.16 g, 4 mmol) for 12 h and worked up as in the earlier cases to give 500 mg (83%) of the unchanged starting material (50), mp 274-275 °C (mixture melting point), after recrystallization from aqueous ethanol).

In a repeat run, 50 (0.6 g, 2 mmol) was treated with potassium (0.16 g, 4 mmol) in THF (125 mL), saturated with

oxygen, for 10 h and worked up in the usual manner to give a residual solid, which was treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a product mixture, which was chromatographed over neutral alumina. Elution with a mixture (2:3) of benzene and petroleum ether gave 400 mg (67%) of the unchanged starting material (50), mp 274-275 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 110 mg (21%) of dibenzamide (21a), mp 144-145 °C (mixture melting point),²⁴ after recrystallization from ethanol.

III.6.12 Reaction of 2,3-Diphenylindole (1a) with Potassium Superoxide. A mixture of 1a (0.54 g, 2 mmol), potassium superoxide (0.29 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred at room temperature for 24 h, protected from light. On completion of the reaction, the mixture was worked up by treatment with water and extraction with aqueous sodium chloride. Removal of the solvent from the organic layer gave a solid, which was chromatographed over neutral alumina. Elution with petroleum ether gave 250 mg (47%) of the unchanged starting material (1a), mp 123-124 °C (mixture melting point). Further elution with petroleum ether gave 160 mg (27%) of 2-benzamidobenzophenone (9a), mp 89-90 °C.

Subsequent elution with a mixture (3:7) of benzene and petroleum ether gave 70 mg (13%) of 9H-dibenzo[a,c]carbazole (8a), mp 192-193 °C (mixture melting point).

III.6.13 Reaction of 2,3-Diphenyl-1-methylindole (1b) with Potassium Superoxide. A mixture of 1b (0.57 g, 2 mmol), potassium superoxide (0.29 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred at room temperature for 24 h and worked up as in the earlier case to give both aqueous and organic fractions. Removal of the solvent from the organic layer gave a residue, which was chromatographed over neutral alumina. Elution with petroleum ether gave 30 mg (5%) of 2,3-diphenylindole (1a), mp 123-124 °C (mixture melting point). Further elution with petroleum ether gave 510 mg (89%) of the unchanged starting material (1b), mp 129-130 °C (mixture melting point).

III.6.14 Reaction of 1,2,3-Triphenylindole (1c) with Potassium Superoxide. A mixture of 1c (0.69 g, 2 mmol), potassium superoxide (0.29 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred at room temperature for 24 h and worked up as in the earlier cases. Removal of the solvent from the organic layer gave a solid, which was chromatographed over neutral alumina. Elution with petroleum

ether gave 40 mg (7%) of 2,3-diphenylindole (1a), mp 123-124 °C (mixture melting point). Further elution with petroleum ether gave 200 mg (29%) of the unchanged starting material (1c), mp 186-187 °C (mixture melting point). Subsequent elution with petroleum ether gave 200 mg (34%) of 2-benzamido-benzophenone (9a), mp 89-90 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether. Continued elution with a mixture (3:7) of benzene and petroleum ether gave 80 mg (11%) of 9-phenyl-9H-dibenzo[a,c]carbazole (8c), mp 196-197 °C (mixture melting point).

III.6.15 Reaction of 2,3,4,5-Tetraphenylpyrrole (10a) with Potassium Superoxide. A mixture of 10a (1.1 g, 3 mmol), potassium superoxide (0.43 g, 6 mmol) and 18-crown-6 (0.79 g, 3 mmol) was stirred at room temperature for 24 h and worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. The aqueous layer, on acidification with dilute hydrochloric acid, gave 47 mg (13%) of benzoic acid (23), mp 120-121 °C (mixture melting point). Removal of the solvent from the organic fraction gave a product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 220 mg (20%) of the unchanged starting material (10a), mp 212-213 °C (mixture melting point). Further elution with a mixture (1:4) of benzene and petroleum

ether gave 170 mg (15%) of 2,3,5,6-tetraphenylpyrazine (33), mp 249-250 °C (mixture melting point). Subsequent elution with a mixture (2:3) of benzene and petroleum ether gave 270 mg (23%) of α -benzoylamino- α' -benzoylstilbene (22a), mp 190-191 °C (mixture melting point). Continued elution with a mixture (1:1) of benzene and petroleum ether gave 50 mg (14%) of benzamide (24a), mp 128-129 °C (mixture melting point). Elution with a mixture (3:2) of benzene and petroleum ether gave 125 mg (11%) of 2,3,4,4-tetraphenyl-2-pyrrolin-5-one (17a), mp 213-214 °C (mixture melting point).

III.6.16 Attempted Reaction of 1,2,3,5-Tetraphenylpyrrole (10b) with Potassium Superoxide. A mixture of 10b (1.1 g, 3 mmol), potassium superoxide (0.43 g, 6 mmol) and 18-crown-6 (0.79 g, 3 mmol) in benzene (100 mL) was stirred for 24 h and worked up as in the earlier cases to give 990 mg (90%) of the unchanged starting material (10b), mp 199-200 °C (mixture melting point), after recrystallization from ethanol.

III.6.17 Attempted Reaction of 1-Benzyl-2,3,5-triphenylpyrrole (10c) with Potassium Superoxide. A mixture of 10c (1.2 g, 3 mmol), potassium superoxide (0.43 g, 6 mmol) and 18-crown-6 (0.79 g, 3 mmol) in benzene (100 mL) was stirred for 24 h and worked up as in the earlier cases to give 1 g

(84%) of the unchanged starting material (10c), mp 166-167 °C (mixture melting point), after recrystallization from ethanol.

III.6.18 Reaction of 2,4,5-Triphenyloxazole (45a) with Potassium Superoxide. A mixture of 45a (0.6 g, 2 mmol), potassium superoxide (0.29 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred for 24 h. The reaction mixture was worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 20 mg (10%) of benzoic acid (23), mp 120-121 °C (mixture melting point). Removal of the solvent from the organic layer gave a residue, which was chromatographed over neutral alumina. Elution with petroleum ether gave 410 mg (68%) of the unchanged starting material (45a), mp 116-117 °C (mixture melting point). Further elution with petroleum ether gave 110 mg (19%) of N-(1,2-diphenylethyl)-benzamide (48a), mp 177-178 °C (mixture melting point), after recrystallization from ethanol.

III.6.19 Reaction of 4,5-Diphenyl-2-methyloxazole (45b) with Potassium Superoxide. A mixture of 45b (0.94 g, 4 mmol) potassium superoxide (0.58 g, 8 mmol) and 18-crown-6 (1.06 g, 4 mmol) in benzene (100 mL) was stirred for 24 h and worked up as in the earlier cases. Acidification of the aqueous layer

with dilute hydrochloric acid gave 60 mg (13%) of benzoic acid (23), mp 120-121 °C (mixture melting point). Workup of the organic layer as in the earlier cases gave a mixture of 500 mg (53%) of the unchanged starting material (45b), bp 210-212 °C (18 mm) and 160 mg (17%) of N-(1,2-diphenylethyl)-acetamide (49b), mp 175-176 °C (mixture melting point).

III.6.20 Reaction of 2,4-Diphenyl-5-methyloxazole (45c) with Potassium Superoxide. A mixture of 45c (0.47 g, 2 mmol), potassium superoxide (0.29 g, 4 mmol), and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred for 24 h and worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 20 mg (9%) of benzoic acid (23), mp 120-121 °C (mixture melting point). Removal of the solvent from the organic fraction gave a residue, which was chromatographed over neutral alumina. Elution with petroleum ether gave 320 mg (64%) of the unchanged starting material (45c), mp 74-75 °C (mixture melting point) and 90 mg (18%) of N-(1-phenyl-1-propenyl)-benzamide (49c), mp 164-165 °C (mixture melting point).

III.6.21 Reaction of 2,4,5-Triphenylimidazole (50) with Potassium Superoxide. A mixture of 50 (0.6 g, 2 mmol),

potassium superoxide (0.14 g, 2 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (100 mL) was stirred for 24 h and worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. Removal of the solvent from the organic fraction gave a residue, which was chromatographed over neutral alumina. Elution with a mixture (2:3) of benzene and petroleum ether gave 310 mg (52%) of the unchanged starting material (50), mp 274-275 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether gave 120 mg (27%) of dibenzamide (21a), mp 144-145 °C (mixture melting point), after recrystallization from ethanol.

III.6.22 Cyclic Voltammetry. Measurements were made with a Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat, a PAR Model 175 Universal Programmer and Kipp and Zonen X-Y recorder. Experiments were performed in a standard three compartment cell, equipped with a Pt-disc working electrode, a Pt-wire counter electrode and a saturated sodium chloride-calomel electrode (SSCE). Cyclic voltammograms were recorded in deaerated acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP).

III.6.23 Pulse Radiolysis. The pulse radiolysis experiments were carried out using a computer controlled apparatus²⁵ and the irradiation was carried out with 5 ns electron pulses

from the Notre Dame 8 MeV ARCO LP-7 linear accelerator, using dose rate of $\sim 2 \times 10^{16}$ eV/g per pulse. The solutions (0.2-0.5 mM) of the substrates were taken in graduated 250 mL cylindrical reservoirs and deaerated by bubbling nitrogen for at least 30 min prior to irradiation. Nitrogen bubbling was continued in the reservoir from which the solution was allowed to flow continuously through the cell (1 cm pathlength). The rate constants for the reactions with solvated electrons (e^-_{sol}) were determined from the kinetic analysis of the enhanced rate of decay of e^-_{sol} in the presence of the substrate or from the growth rate of the radical anion.

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CHAPTER IV

ELECTRON TRANSFER REACTIONS. REACTION OF TETRACYCLONE, FURANS AND RELATED SUBSTRATES WITH POTASSIUM

IV.1 ABSTRACT

Potassium-induced transformations of tetracyclone (1), tetraphenylfuran (6a), 2,5-diphenylfuran (6b), 2,3,5-triphenylfuran (6c), 2,3-diphenylindenone (31), and 2,3-diphenylbenzofuran (47) have been studied. The reaction of 1 with potassium has been reinvestigated and it has been shown that when the reaction is carried out in THF, saturated with oxygen, a mixture of products consisting of tetraphenylfuran (6a), cis-dibenzoylstilbene (7), benzoic acid (17), and 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (18) is formed. The reaction of 1 with potassium superoxide, on the other hand, gave a moderate yield of 3,4,5,6-tetraphenyl-2-pyranone (15, 23%), besides 6a, 7, 17 and 18. The reaction of tetraphenylfuran (6a) itself with potassium in THF, saturated with oxygen gave a mixture of cis-dibenzoylstilbene (7), 3-benzoyl-2,3-diphenyl-2-hydroxy-1-indanone (26), 2,3-diphenyl-1-indenone (31), and 1,2,3,4-tetraphenylbutan-1-one (32a). The reaction of 2,5-diphenylfuran

(6b) with potassium in THF gave benzoic acid (17) as the only isolable product, whereas 2,3,5-triphenylfuran (6c), under analogous conditions gave a mixture of benzoic acid (17), 1,3,4-triphenylbutan-1-one (32c), 2-hydroxy-1,3,4-triphenylbutan-1,4-dione (37c), and 1,2,4-triphenylbutan-1,4-dione (38c). A similar mixture of products was obtained when the reaction of 6c was carried out with potassium in THF, saturated with oxygen. In contrast, the attempted reactions of 6a-c with potassium superoxide did not give any isolable product; most of the starting material was recovered unchanged, in each case. The reaction of 2,3-diphenyl-1-indenone (31) with potassium in THF, saturated with oxygen gave a mixture of benzoic acid (17), dibenzo[a,c]-13-fluorenone (44), 2,3-diphenylbenzofuran (47), and 2,3-diphenyl-2-hydroxyindanone (48). A similar mixture of products was obtained when the reaction of 31 was carried out with potassium superoxide. An attempted reaction of 2,3-diphenylbenzofuran (47) with potassium did not give any product; most of the starting material could be recovered unchanged.

Reasonable mechanisms have been suggested to account for the formation of the various products in the reaction of 1, 6a-c, 31 and 47 with potassium in THF. Cyclic voltammetric studies have been carried out to measure the reduction potentials of 1, 6a-c, 31 and 47 in the generation of their radical anions. The radical anions of these substrates have also been

generated through pulse radiolysis in methanol and their spectra showed absorption maxima in the region 320-380 nm.

IV.2 INTRODUCTION

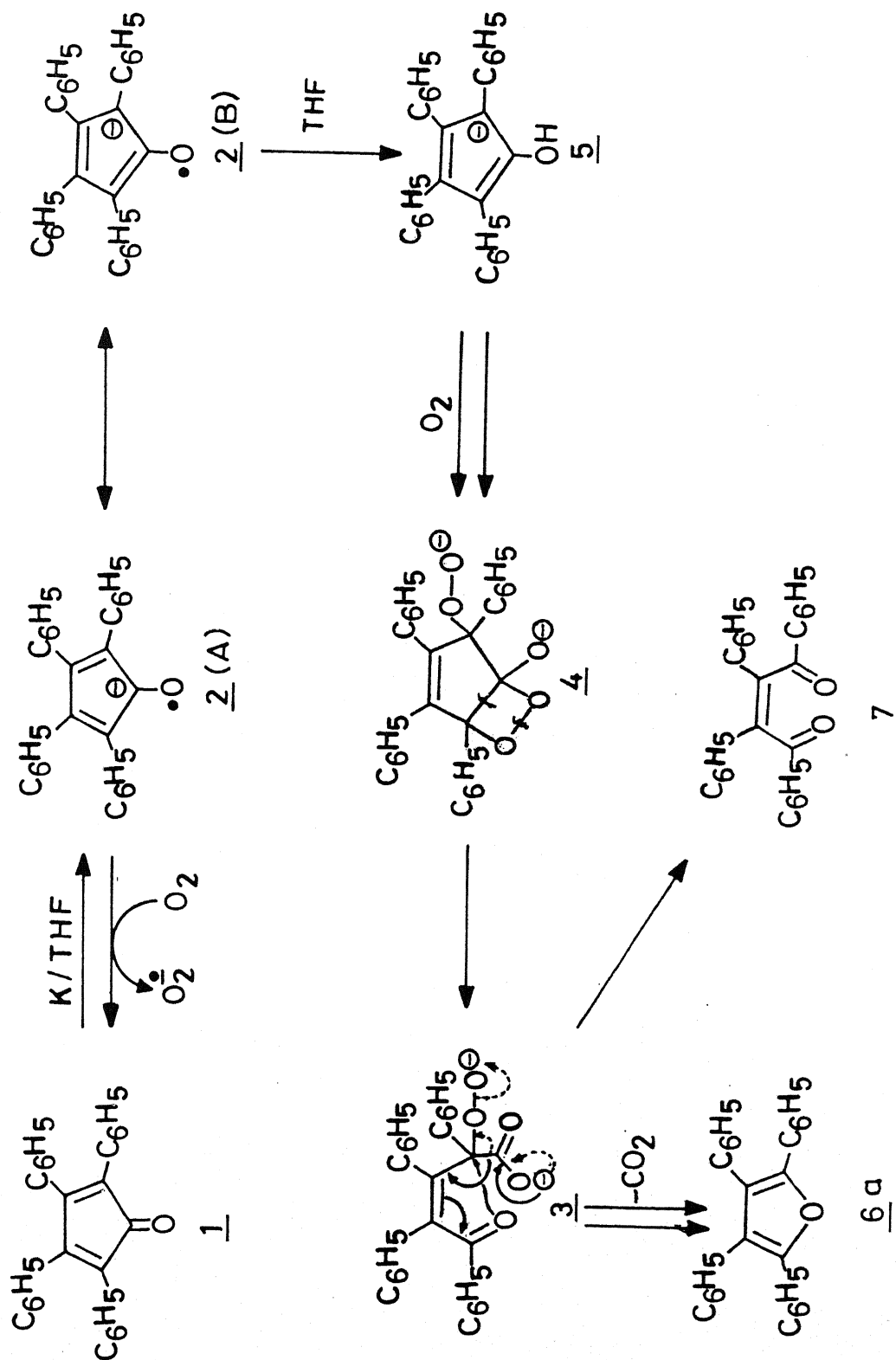
An earlier report¹ from this laboratory had indicated that tetracyclone (1), on treatment with potassium in THF gives a mixture of tetraphenylfuran (6a, 10%), cis-dibenzoylstilbene (7, 21%), and benzoic acid (17, 10%), whereas, 6a, under analogous conditions gives a mixture of 2,3-diphenylindenone (31, 18%) and a few unidentified products. Similarly, it has been reported that the reaction of 31 with potassium in THF gives a mixture of dibenzo[a,c]-13-fluorenone (44, 29%) and 2,3-diphenyl-2-hydroxyindanone (48, 25%). In order to rationalize the formation of these oxygenated products in the reaction of tetracyclone (1) and related substrates, we have reinvestigated the reaction of these substrates with potassium under different conditions and with potassium superoxide.

IV.3 RESULTS AND DISCUSSION

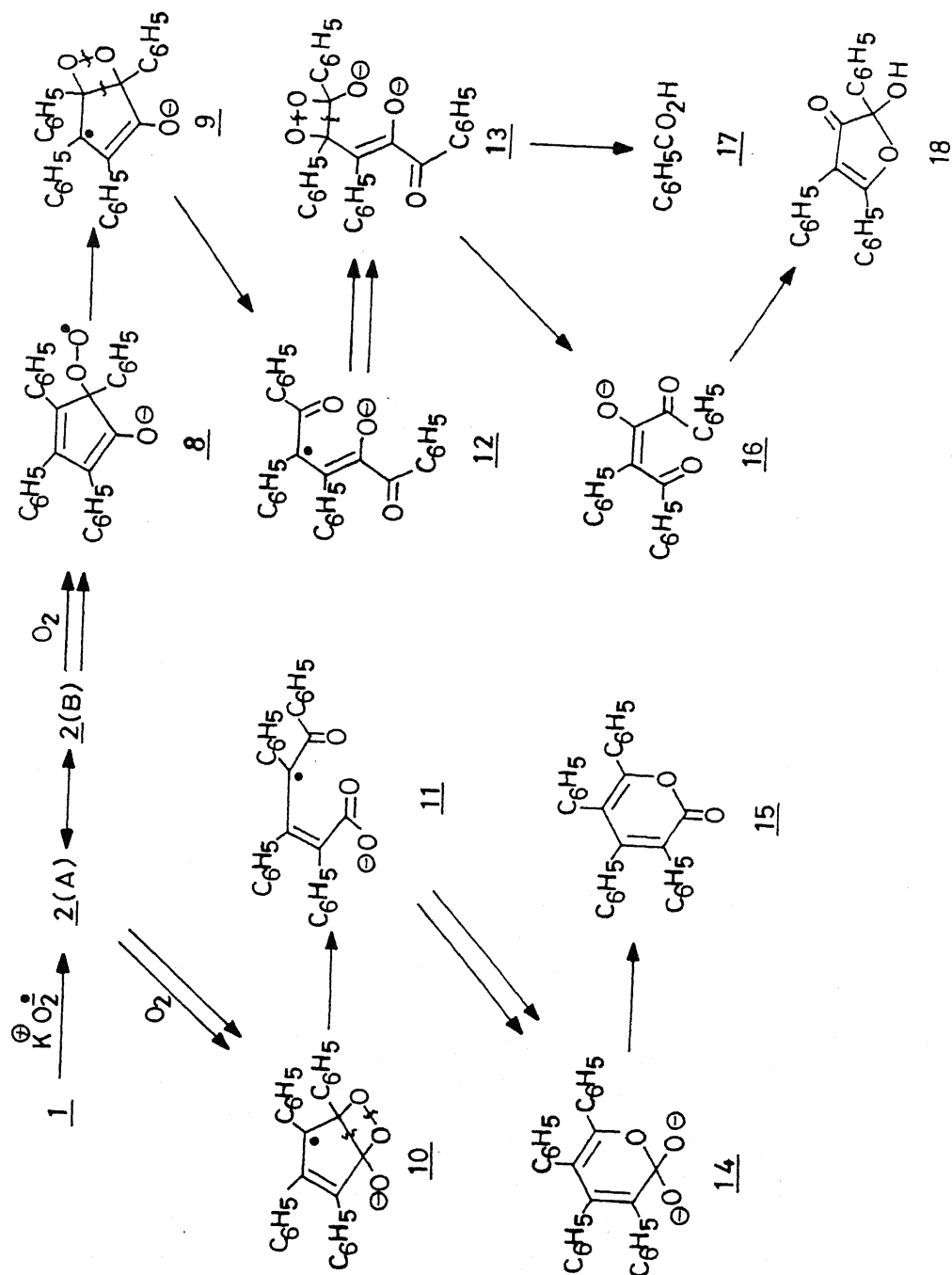
The substrates that we have examined in the present investigation include, tetracyclone (1), tetraphenylfuran (6a), 2,5-diphenylfuran (6b), 2,3,5-triphenylfuran (6c), 2,3-diphenyl-1-indenone (31), and 2,3-diphenylbenzofuran (47). The reaction of 1 with potassium in THF, saturated with oxygen, for example,

gave a mixture of products consisting of tetraphenylfuran (6a, 12%), cis-dibenzoylstilbene (7, 5%), benzoic acid (17, 53%), and 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (18, 8%). Earlier reports² had stated that the oxidation of 1 with potassium superoxide leads to a mixture of 17, 18, and 3,4,5,6-tetraphenylpyran-2-one (15). To examine whether any tetraphenylfuran 6a is formed under these circumstances, we have reinvestigated this reaction. Treatment of 1 with excess of potassium superoxide and 18-crown-6 in benzene for 30 h gave a small yield of 6a, besides 15, 17 and 18. The formation of the different products in the reaction of 1 with potassium in THF could be understood in terms of the pathways shown in Schemes IV.1 and IV.2. It is assumed that the initial step in the reaction involves the formation of the radical anion 2, which can abstract a hydrogen atom from the solvent to give the anionic species 5. Further reaction of 5 with oxygen, under workup conditions, will give the hydroperoxy dioxetane intermediate 4, which can undergo subsequent transformations to give 6a and 7, as shown in Scheme IV.1. The initially formed radical anion intermediate 2, on the otherhand, could also lead to the dioxetane intermediates 9 and 10, through reaction with oxygen. The dioxetane intermediate 9, for example, will lead to a mixture of benzoic acid (17) and 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (18), whereas 10 will lead to 3,4,5,6-tetraphenylpyran-2-one (15), as shown in Scheme IV.2. The

Scheme IV.1



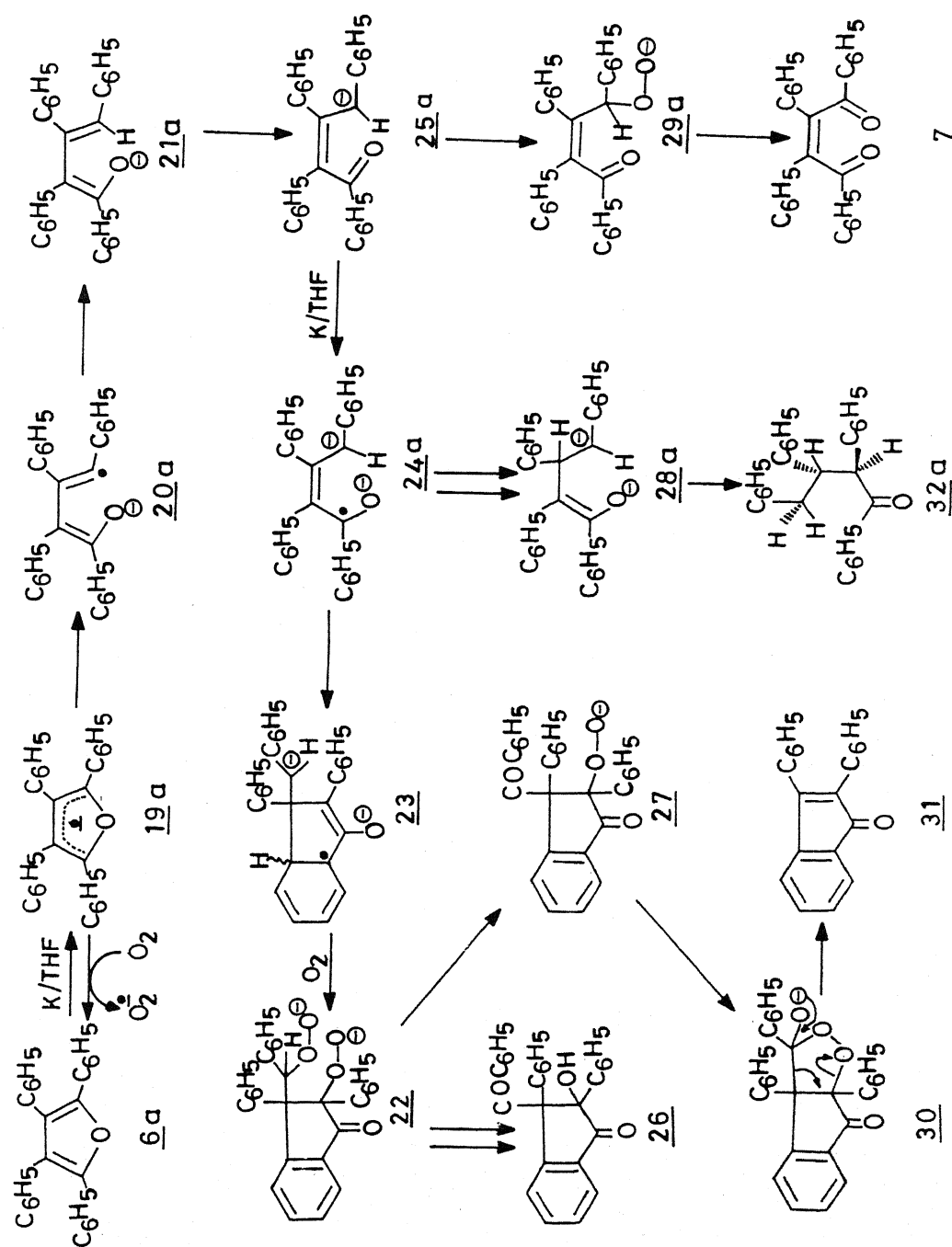
Scheme IV.2



involvement of oxygen in the reaction of the radical anion 2, as suggested in Scheme IV.2 is supported by the observation that similar products are formed in the reaction of 1 with potassium superoxide.

With a view to examining whether any of the products isolated from the reaction of 1 with potassium in THF, arises through the reaction of tetraphenylfuran (6a) with potassium in subsequent steps, we have studied this reaction separately. Treatment of 6a with excess of potassium in THF gave a mixture of cis-dibenzoylstilbene (7, 5%), 3-benzoyl-2,3-diphenyl-2-hydroxy -1-indanone (26, 35%), 2,3-diphenyl-1-indenone (31, 18%), and 1,2,3,4-tetraphenylbutan-1-one (32a, 25%), along with some recovered starting material (6a, 12%). When the reaction of 6a with potassium was carried out in oxygen-saturated THF, the product mixture consisted of 7 (10%), 31 (14%), and 26 (53%); however, the yield of 26 in this case was higher. On the other-hand, when the reaction of 6a with potassium superoxide was carried out in benzene containing 18-crown-6, practically no reaction occurred; most of the starting material could be recovered unchanged. The formation of products such as 7, 26, 31, and 32a from 6a could be rationalized in terms of the pathway shown in Scheme IV.3. The initial step in the reaction would involve the formation of the radical anion intermediate 19a, which can undergo ring opening, followed by abstraction of

Scheme IV.3



hydrogen atom from the solvent to give the anion intermediate 25a. Further transformation of 25a through its reaction with oxygen will lead to 7, as shown in Scheme IV.3. The anionic species 25a, on the otherhand, could undergo further reduction to give the intermediate 24a, which can ultimately lead to the reduction product 32a, or the oxygenated products such as 26 and 31, as shown in Scheme IV.3. The involvement of oxygen in the formation of 26, for example, as suggested in Scheme IV.3 is supported by the observation that it is formed in greater amounts at the expense of 32a, when the reaction of 6a is carried out in THF, saturated with oxygen. The absence of products such as 7, 26, 31, and 32a in the reaction of 6a with potassium superoxide, on the otherhand, would imply that the initial electron transfer from superoxide to 6a is not taking place to generate the radical anion 19a. Our cyclic voltammetric studies (see, later) reveal that the reduction potential of 6a is considerably higher than that of tetrayclone 1 and hence it is not surprising that electron transfer does not occur from superoxide to 6a.

To ascertain whether aryl substituents in the furan ring have any effect on the potassium induced transformation of furans, we have examined the reaction of 2,5-diphenylfuran (6b) and 2,3,5-triphenylfuran (6c) with potassium in THF. Thus, treatment of 6b with potassium in THF gave a 46% yield of

benzoic acid (17), along with a 33% recovery of the unchanged starting material (6b), whereas, 6c, under analogous conditions gave a mixture of benzoic acid (17, 14%), 1,3,4-triphenylbutan-1-one (32c, 21%), 2-hydroxy-1,3,4-triphenylbutan-1,4-dione (37c, 11%), and 1,3,4-triphenylbutan-1,4-dione (38c, 9%). The reaction of 6b with potassium in THF, saturated with oxygen, however, did not give any isolable product; most of the starting material could be recovered unchanged (6b, 88%). In contrast, the reaction of 6c with potassium in THF, saturated with oxygen gave a mixture of 17 (25%), 32c (5%), 37c (17%), and 38c (13%). As in the case of 6a, the reaction of 6b and 6c with potassium superoxide in benzene containing 18-crown-6 did not give rise to any isolable product; most of the starting material could be recovered unchanged, in each case.

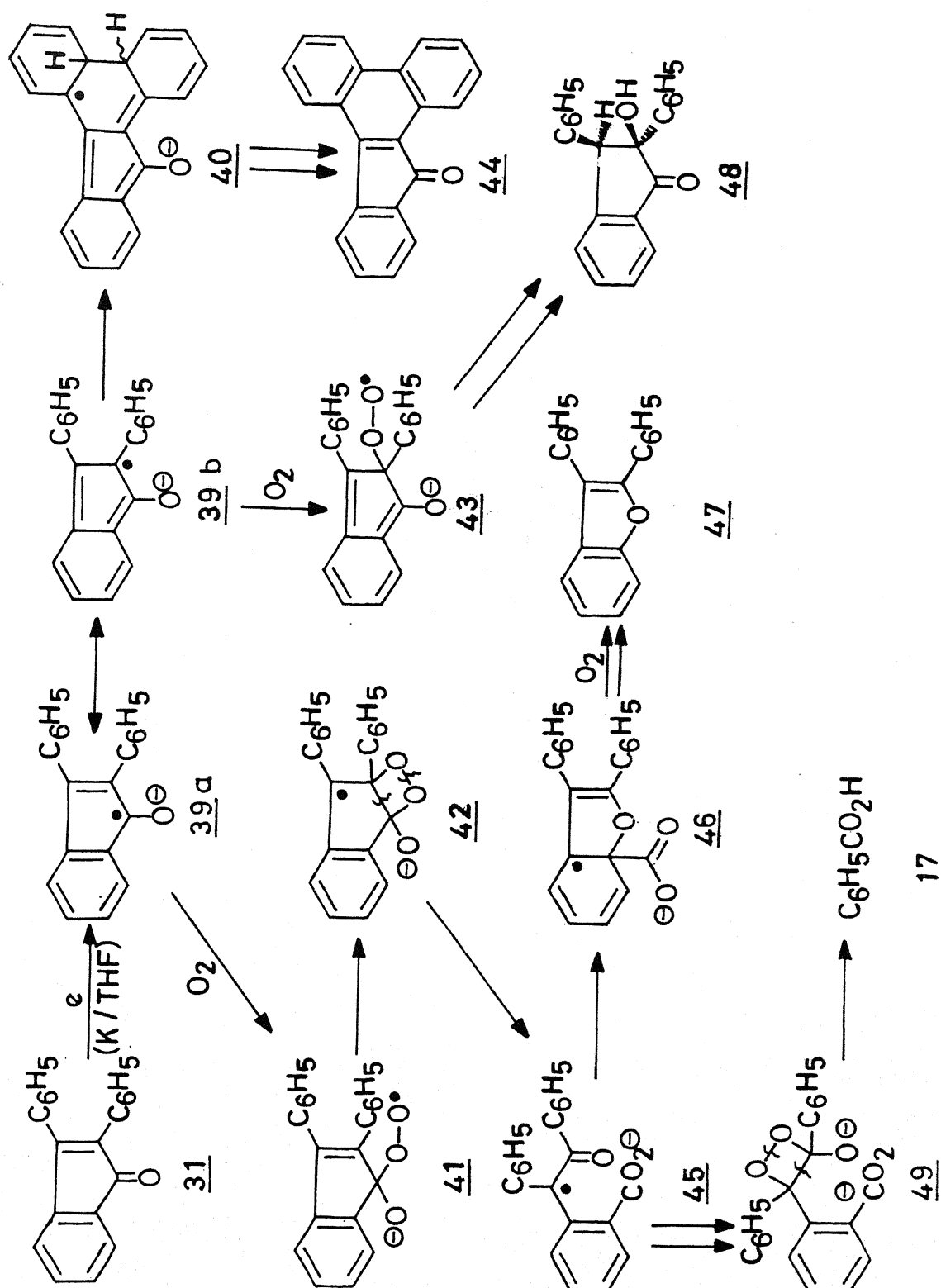
The formation of benzoic acid (17) from 6b and products such as 17, 32c, 37c, and 38c from 6c, on treatment with potassium in THF could be explained in terms of the pathways shown in Scheme IV.4. The formation of 17 from both 6b and 6c could arise through the reactions of the initially formed anionic species 21b and 21c, respectively, whereas products such as 32c, 37c, and 38c could arise from the dianion intermediate 28c, as shown in Scheme IV.4.

In order to assess whether any of the products in the reaction

of tetracyclone (1) with potassium arises through an intermediate precursor such as 2,3-diphenyl-1-indenone (31), we have examined the reaction of 31 with potassium in a separate experiment. Thus, treatment of 31 with potassium in THF, saturated with oxygen gave a mixture of benzoic acid (17, 5%), dibenzo[a,c]-13-fluorenone (44, 33%), 2,3-diphenylbenzofuran (47, 2%), and 2,3-diphenyl-2-hydroxy-1-indanone (48, 30%), along with some unchanged starting material (31, 3%). It may be pointed out here that the reaction of 31 with potassium in THF, in the absence of oxygen saturation is reported¹ to give a mixture of products consisting of 17 (4%), 44 (29%), 47 (2%), and 48 (25%). A similar mixture of products consisting of 17 (46%), 44 (7%), 47 (2%), and 48 (3%) was also observed in the reaction of 31 with potassium superoxide in benzene containing 18-crown-6.

The formation of the different products in the reaction of 31 with potassium in THF may be understood in terms of the pathways shown in Scheme IV.5. The fact that the same product mixture is obtained, in the reaction of 31 with potassium in oxygen-saturated THF or with potassium superoxide, supports the suggested pathway, involving the initial formation of the radical anion intermediate 39 and its subsequent reaction with oxygen. The fact that a higher yield of benzoic acid (17) and lower yields of 44 and 48 were observed in the reaction of 31 with potassium superoxide would suggest that oxidative pathways

Scheme IV.5



involving dioxetane intermediates such as 42 and 49 may become predominant under these conditions.

It is evident that none of the products formed in the reaction of 31 with potassium arises through the intermediacy of 2,3-diphenylbenzofuran (47), since we have shown, in a separate experiment, that treatment of 47 with potassium in THF does not lead to any isolable product; most of the starting material is recovered unchanged under these conditions.

IV.4 CYCLIC VOLTAMMETRIC STUDIES³

In the present study, we have generated electrochemically the radical anions of tetracyclone (1), tetraphenylfuran (6a), 2,5-diphenylfuran (6b), 2,3,5-triphenylfuran (6c), 2,3-diphenyl-1-indenone (31), and 2,3-diphenylbenzofuran (47). The cyclic voltammograms of 1, 6a-c, 31, and 47 are shown in Figure IV.1 and reduction and oxidation potentials are summarized in Table IV.1. The substrates 1 and 6a-c exhibited reversible reduction peaks with reduction potentials in the range of -0.915 to -2.5 V versus SSCE. On the otherhand, substrates 31 and 47 underwent irreversible reduction with half peak potentials at -1.1 and -2.55 V versus SSCE, respectively. By taking the case of 1 as a representative example, it has been possible to show that the radical anions generated from the substrates under study are quenched by oxygen. In

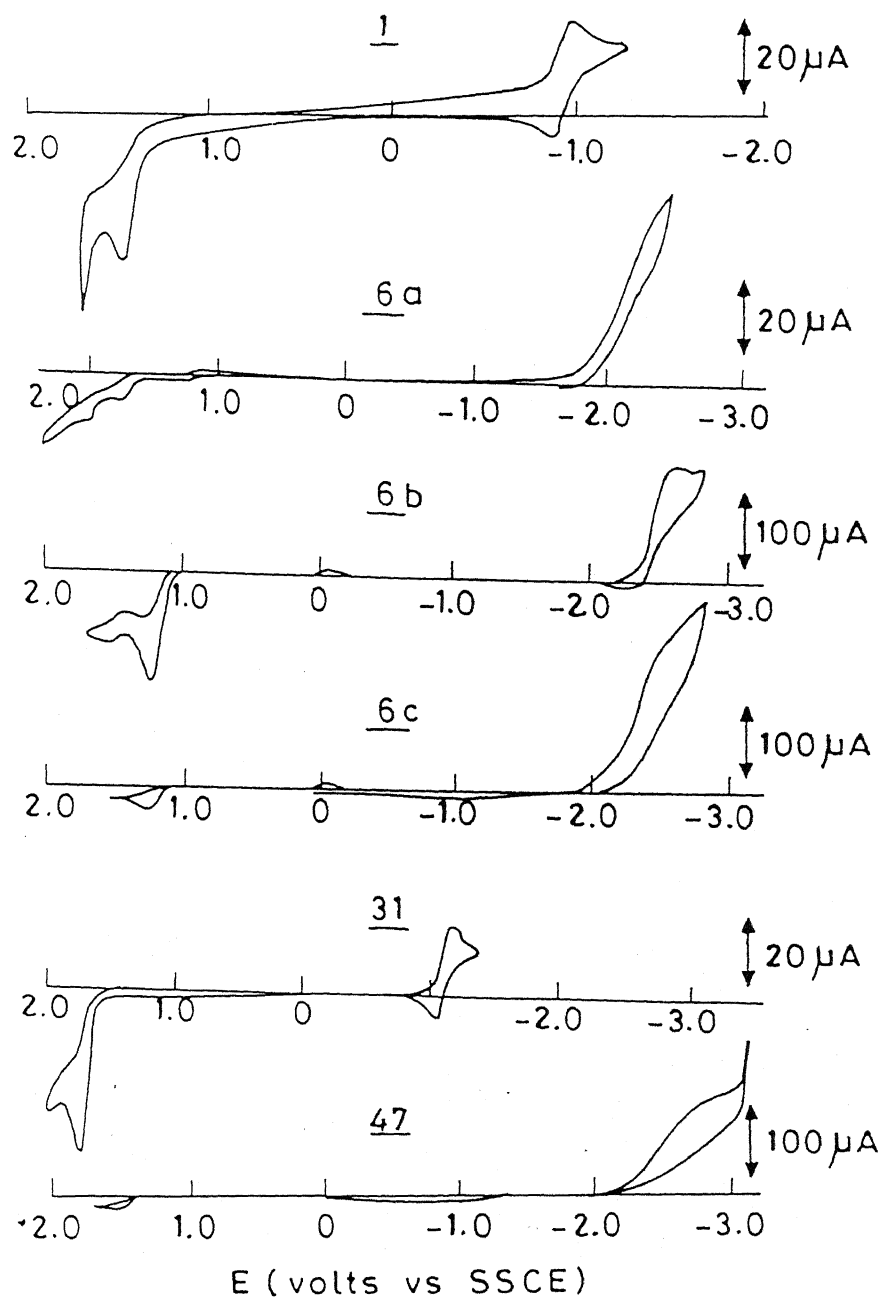


Figure IV.1 Cyclic voltammograms of 1, 6a-c, 31 and 47

Table IV.1 Electrochemical, spectral and kinetic data of tetracyclone (1), furans (6a-c), indenone (31) and benzofuran (47)

| Substrate | Electrochemical characteristics ^a | | Absorption maxima (nm) | | k_f $10^9 \text{ M}^{-1} \text{ s}^{-1}$ | $\tau_{1/2e}$ ms | |
|-----------|--|---------------------------------------|------------------------|---------------------------------|---|---------------------|-------------------------------|
| | $E_p/2$ (oxidation) | $E_p/2$ (reduction) (V vs SSCE) | Starting material | Radical anion | | | |
| | | | | Potassium reaction ^c | | | Pulse radiolysis ^d |
| <u>1</u> | 1.40 | -0.88 (-0.915) ^b | 363, 340, 510 | 285, 330, 405 | 8.8 | 0.027 | |
| <u>6a</u> | 1.20 (1.23) ^b | -2.20 | 325 | 375 | 4.2 | 3.800 | |
| <u>6b</u> | 1.17 | -2.44 (-2.47) | 225, 323 | --- | 0.15 \pm 0.01 | 2.42 \pm 0.1 | |
| <u>6c</u> | 1.18 | -2.50 | 230, 323 | --- | 2.95 \pm 0.05 | 5.57 \pm 0.3 | |
| <u>31</u> | 1.67 | -1.07 (-1.1) ^b | 433 | 375 | 18.3 | 0.0044 | |
| <u>47</u> | 1.45 | -2.55 | 253, 302 | --- | 0.19 \pm 0.09 | 7.6 \pm 0.3 | |

a) In acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate.

a) In acetonitrile containing 0.1 M tetrabutylammonium perchlorate. b) The values in parentheses are the standard oxidation or reduction potentials as obtained from the reversible cyclic voltammograms. c) In THF. d) In methanol. e) Half-life of the radical anion in methanol. f) Rate constant for the reaction of the substrate with solvated electron in methanol.

a deaerated solution, for example, the radical anion of 1 exhibited reversible oxidation, upon reversal of the cyclic voltammetric scan, as shown in Figure IV.2. However, on introduction of a small amount of oxygen into the system, a change in the cyclic voltammetric behaviour was observed. The substrate exhibited only a cathodic peak, corresponding to the reduction of 1 to its radical anion. The anodic peak representing the oxidation of the radical anion was not observed, indicating thereby the quenching of the radical anion by oxygen. This observation supports the reaction pathways outlined in Schemes IV.1-IV.5, implicating the reaction of the initially formed radical anions of the different substrates with oxygen and their subsequent transformations to give the observed products.

IV.5 PULSE RADIOLYSIS STUDIES⁴

It has been reported earlier that radical anions of unsaturated organic compounds can be generated through the reaction with solvated electron (e^-_{sol}) in polar solvents such as methanol under pulse radiolytic conditions.⁵⁻⁸ In the present investigation, the radical anions of 1, 6a-c, 31, and 47 were generated in methanol pulse radiolytically and their spectra are presented in Figure IV.3. These radical anions showed strong absorption maxima in the region of 320-380 nm and had a halflife of 4.4-7.6 μs in methanol. It

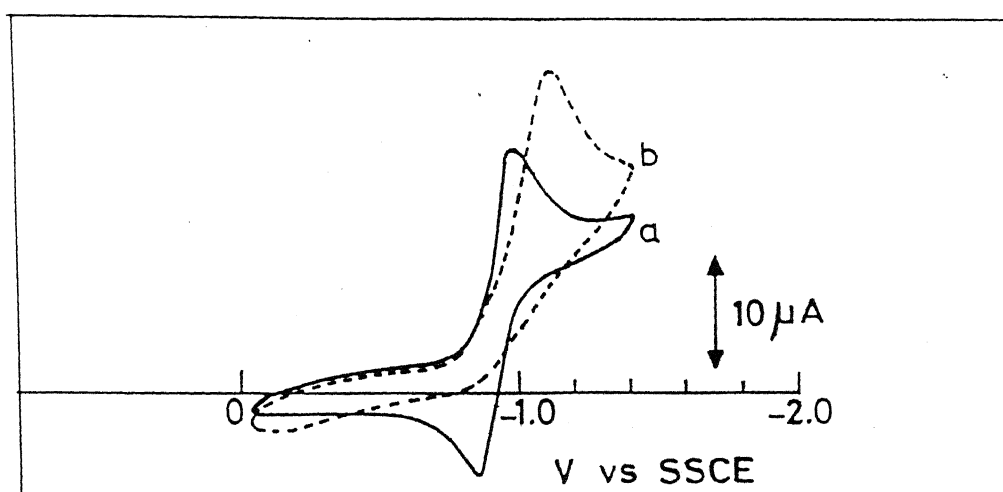


Figure IV.2 Cyclic voltammograms of 1; curve a, in nitrogen saturated solution, and curve b, after introduction of oxygen into the system

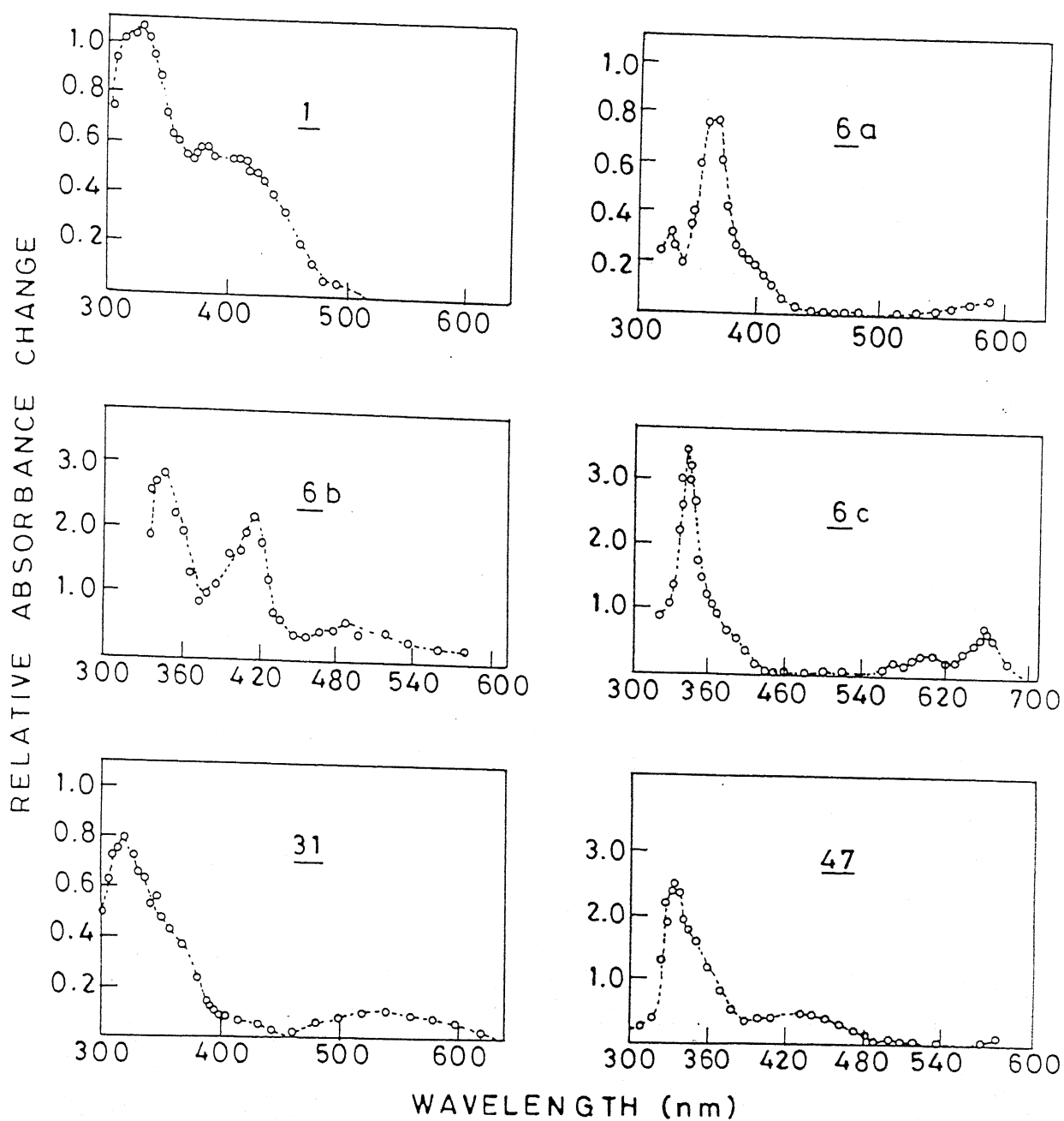


Figure IV.3 Absorption spectra of the pulse radiolytically generated radical anions from 1, 6a-c, 31 and 47

is pertinent to point out that these spectral characteristics closely matched the spectral characteristics of the intermediates, formed on shaking 1, 6a-c, 31, and 47, respectively with potassium in THF, justifying our assumption that the radical anions are the primary intermediates formed through electron transfer process in the reaction of these substrates with potassium in THF. The rate constants for the reaction of solvated electron with these substrates in methanol under pulse radiolysis reveal that they are formed under diffusion controlled rates.

IV.6 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 219 or Beckman DB spectrophotometers. The ^1H NMR traces were recorded on Varian EM-390 or Nicolet NB 300 NMR spectrometers, whereas ^{13}C NMR spectra were recorded on a Bruker 400 NMR spectrometer, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single-focussing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. The petroleum ether used was the fraction with bp 60-80 °C. THF was dried over sodium and distilled before use. Gold Label

(Aldrich) acetonitrile was used for cyclic voltammetric studies and spectral grade methanol (Fischer Scientific) was used for pulse radiolysis.

IV.6.1 Starting Materials. Tetracyclone (1),⁹ mp 219-220°C, tetraphenylfuran (6a),¹⁰ mp 173-174 °C, 2,5-diphenylfuran (6c),¹² mp 95-96 °C, 2,3-diphenyl-1-indenone (31),¹³ mp 151-152 °C, and 2,3-diphenylbenzofuran (47),¹⁴ mp 120-121 °C, were prepared by reported procedures.

IV.6.2 Reaction of Tetracyclone (1) with Potassium in THF, Saturated with Oxygen. A mixture of 1 (0.96 g, 2.5 mmol) and finely cut potassium (0.2 g, 5 mmol) in THF (125 mL), saturated with oxygen, was shaken in a Schlenk tube for 12 h. A few broken glass pieces were added to the reaction mixture to ensure a clean surface of the metal throughout the reaction. The reaction mixture was poured into moist THF (125 mL) to destroy any unchanged potassium and the solvent was removed under vacuum. The residue was treated with water (10 mL) and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid and extraction with benzene gave 160 mg (53%) of benzoic acid (17), mp 120-121 °C (mixture melting point).

Removal of the solvent from the methylene chloride-extract

gave a residue, which was chromatographed over silica gel. Elution with petroleum ether gave 110 mg (12%) of tetraphenylfuran (6a), mp 173-174 °C (mixture melting point), after recrystallization from ethanol. Further elution with a mixture (1:9) of benzene and petroleum ether gave 140 mg (15%) of the unchanged starting material (1), mp 219-220 °C (mixture melting point). Subsequent elution with a mixture (3:7) of benzene and petroleum ether gave 46 mg (5%) of cis-dibenzoylstilbene (7), mp 214-215 °C (mixture melting point),¹⁵ after recrystallization from ethanol. Continued elution with benzene gave 65 mg (8%) of 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (18), mp 198-199 °C (mixture melting point),¹⁶ after recrystallization from a mixture (1:2) of benzene and petroleum ether.

IV.6.3 Reaction of Tetraphenylfuran (6a) with Potassium in THF. A mixture of 6a (0.93 g, 2.5 mmol) and potassium (0.2 g, 5 mmol) in THF (125 mL) was shaken for 10 h and worked up by treatment with moist THF and removal of the solvent under vacuum to give a residue, which was treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave a product mixture, which was chromatographed over silica gel. Elution with petroleum ether gave 107 mg (12%) of the unchanged starting material (6a), mp 173-174 °C (mixture melting point), after recrystallization

from ethanol. Further elution with a mixture (1:9) of benzene and petroleum ether gave 130 mg (18%) of 2,3-diphenyl-1-indenone (31), mp 151-152 °C (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 230 mg (25%) of 1,2,3,4-tetraphenylbutan-1-one (32a), mp 197-198 °C (mixture melting point),¹⁷ after recrystallization from a mixture (1:4) of benzene and petroleum ether. Further elution with a mixture (2:3) of benzene and petroleum ether gave 50 mg (5%) of cis-dibenzoylstilbene (7), mp 214-215 °C, (mixture melting point),¹⁵ after recrystallization from ethanol. Continued elution with a mixture (2:3) of benzene and petroleum ether gave 350 mg (35%) of 3-benzoyl-2,3-diphenyl-2-hydroxy-1-indanone (26), mp 253-254 °C, after recrystallization from a mixture (4:1) of benzene and cyclohexane.

IR spectrum ν_{\max} (KBr): 3505 (OH), 3065 and 3025 (CH), 1685 (C=O), and 1595 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 258 nm (ϵ , 8200) and 302 (1300).

^1H NMR spectrum (CDCl_3): δ 3.0 (s, 1 H, OH, D_2O -exchangeable), 6.55-8.10 (m, 19 H, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 70.00 (s), 75.12 (s), 126.01 (d), 126.71 (d), 127.06 (d), 127.30 (d), 127.38 (d),

127.55 (d), 127.80 (d), 127.82 (s), 127.88 (d), 128.33 (d), 128.44 (d), 128.96 (s), 129.60 (d), 130.32 (s), 131.71 (d), 134.65 (d), 141.87 (s), 144.88 (s), and 193.87 (s) (C=O).

Mass spectrum, m/e (relative intensity): 404 (M^+ , 0.1), 387 ($M^+ - OH$, 1), 327 ($M^+ - C_6H_5$, 0.1), 299 ($M^+ - COC_6H_5$, 100), 282 ($M^+ - COC_6H_5, - OH$, 24), 250 (16), 222 ($M^+ - COC_6H_5, - C_6H_5$, 10), 209 (8), 193 (5), 165 (12), 152 (8), 105 ($C_6H_5CO^+$, 44), 77 ($C_6H_5^+$, 40), and other peaks.

Anal. Calcd for $C_{28}H_{20}O_3$: C, 83.17; H, 4.95. Found : C, 83.83; H, 5.40.

In a repeat experiment, a mixture of 6a (0.93 g, 2.5 mmol) in THF (125 mL), saturated with oxygen, was shaken with potassium (0.2 g, 5 mmol) for 10 h and worked up as in the earlier case to give a mixture of 175 mg (19%) of the unchanged starting material (6a), mp 173-174 °C (mixture melting point), 100 mg (14%) of 31, mp 151-152 °C (mixture melting point), 100 mg (10%) of 7, mp 214-215 °C (mixture melting point), and 400 mg (53%) of 26, mp 253-254 °C (mixture melting point).

IV.6.4 Reaction of 2,5-Diphenylfuran (6b) with Potassium in THF. A mixture of 6b (1 g, 5 mmol) and potassium (0.39 g, 10 mmol) in THF (125 mL) was shaken for 15 h and worked up by treatment with moist THF and removal of the solvent under reduced pressure to give a residual mass, which was subsequently

treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 250 mg (46%) of benzoic acid (17), mp 120-121 °C (mixture melting point). Removal of the solvent from the organic layer gave 330 mg (33%) of the unchanged starting material (6b), mp 89-90 °C (mixture melting point), after recrystallization from ethanol.

In a repeat run, treatment of 6b (1 g, 5 mmol) with potassium (0.39 g, 10 mmol) in THF (125 mL), saturated with oxygen, for 15 h and workup as in the earlier cases gave 880 mg (88%) of the unchanged starting material (6b), mp 89-90 °C (mixture melting point).

IV.6.5 Reaction of 2,3,5-Triphenylfuran (6c) with Potassium in THF. A mixture of 6c (1.48 g, 5 mmol) and potassium (0.39 g, 10 mmol) in THF (125 mL) was shaken for 10 h and worked up as in the earlier cases by treatment with moist THF and removal of the solvent under vacuum to give a solid material, which was subsequently treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave 80 mg (14%) of benzoic acid (17), mp 120-121 °C (mixture melting point).

Removal of the solvent from the organic layer gave a residue, which was chromatographed over silica gel. Elution

with petroleum ether gave 110 mg (7%) of the starting material (6c), mp 95-96 °C (mixture melting point), after recrystallization from ethanol. Further elution with a mixture (1:4) of benzene and petroleum ether gave 320 mg (21%) of 1,3,4-triphenylbutan-1-one (32c), mp 112-113 °C (mixture melting point),¹⁸ after recrystallization from ethanol. Subsequent elution with a mixture (3:2) of benzene and petroleum ether gave 140 mg (9%) of 1,3,4-triphenylbutan-1,4-dione (38c), mp 126-127 °C (mixture melting point),¹⁹ after recrystallization from ethanol. Continued elution with benzene gave 120 mg (7%) of 2-hydroxy-1,3,4-triphenylbutan-1,4-dione (37c), mp 185-186 °C, after recrystallization from ethanol.

IR spectrum ν_{\max} (KBr): 3260 (OH), 3060 (CH), 1685 (C=O), 1610 and 1590 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 230 nm (ϵ , 20,500) and 290 (350).

^1H NMR spectrum (CDCl_3): δ 5.25 (d, 1 H, methine), 5.65 (q, 1 H, the quartet is changed to a doublet after D_2O -shake), 7.0-8.0 (m, 15 H, aromatic), and 8.45 (d, 1 H, OH, D_2O -exchangeable).

Mass spectrum, m/e (relative intensity): 330 (M^+ , 1), 329 (12), 328 (2), 327 (2), 312 ($\text{M}^+ - \text{H}_2\text{O}$, 3), 310 (6), 301 (1), 300 (6), 225 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 6), 224 (28), 105 (99), and 77 (100).

Anal. Calcd for $C_{22}H_{18}O_3$: C, 80.00; H, 5.45. Found: C, 80.24; H, 5.36.

In a repeat run, a mixture of 6c (1.48 g, 5 mmol) and potassium (0.39 g, 10 mmol) in THF (125 mL), saturated with oxygen, was shaken for 10 h and worked up as in the earlier case to give a mixture of 80 mg (5%) of 32c, mp 112-113 °C (mixture melting point), 200 mg (13%) of 38c, mp 126-127 °C (mixture melting point), 280 mg (17%) of 37c, mp 185-186 °C, 150 mg (25%) of 17, mp 120-121 °C (mixture melting point), and 40 mg (3%) of the unchanged starting material (6c), mp 95-96 °C (mixture melting point).

IV.6.6 Reaction of 2,3-Diphenyl-1-indenone (31) with Potassium in THF. Treatment of 31 (1.12 g, 4 mmol) with potassium (0.47 g, 12 mmol) in THF (125 mL) for 12 h and workup by pouring into moist THF and removal of the solvent under vacuum gave a residual solid, which was subsequently treated with water and extracted with methylene chloride. Acidification of the aqueous layer with dilute hydrochloric acid gave a solid, which was recrystallized from a mixture (1:9) of benzene and petroleum ether to give 25 mg (5%) of benzoic acid (17), mp 120-121 °C (mixture melting point). Removal of the solvent from the methylene chloride-extract gave a residue, which was chromatographed over silica gel. Elution with

petroleum ether gave 20 mg (2%) of 2,3-diphenylbenzofuran (47), mp 120-121 °C (mixture melting point),¹⁴ after recrystallization from ethanol. Further elution with a mixture (1:9) of benzene and petroleum ether gave 30 mg (3%) of the unchanged starting material (31), mp 151-152 °C (mixture melting point). Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 370 mg (33%) of dibenzo[a,c]-13-fluorenone (44), mp 186-187 °C (mixture melting point)²⁰ after recrystallization from a mixture (1:4) of benzene and petroleum ether. Further elution with a mixture (1:1) of benzene and petroleum ether gave 360 mg (30%) of 2,3-diphenyl-2-hydroxy-1-indanone (48), mp 128-129 °C (lit. mp 129-130 °C),²¹ after recrystallization from a mixture (1:2) of benzene and petroleum ether.

In a repeat run, 1.12 g (4 mmol) of 31 was treated with 0.32 g (8 mmol) of potassium in 125 mL of THF, saturated with oxygen, for 10 h and worked up as in the earlier case to give 165 mg (34%) of 17, mp 120-121 °C (mixture melting point), 25 mg (2%) of 47, mp 120-121 °C (mixture melting point), 80 mg (7%) of the recovered starting material (31), mp 151-152 °C (mixture melting point), 175 mg (16%) of 44, mp 186-187 °C, and 125 mg (11%) of 48, mp 128-129 °C.

IV.6.7 Reaction of 2,3-Diphenylbenzofuran (47) with Potassium in THF. A mixture of 47 (0.56 g, 2 mmol) and

potassium (0.16 g, 4 mmol) in THF (125 mL) was shaken for 10 h and worked up by treatment with moist THF and removal of the solvent under vacuum to give a residual solid, which was subsequently treated with water and extracted with methylene chloride. Removal of the solvent from the methylene chloride-extract gave 400 mg (72%) of the unchanged starting material (47), mp 120-121 °C (mixture melting point), after recrystallization from ethanol.

In a repeat run, treatment of 47 (0.56 g, 2 mmol) with potassium (0.16 g, 4 mmol) in THF (125 mL), saturated with oxygen, for 10 h and workup as in the earlier cases gave 390 mg (69%) of the unchanged starting material (47), mp 120-121 °C (mixture melting point).

IV.6.8 Reaction of Tetracyclone (1) with Potassium Superoxide. A mixture of 1 (0.768 g, 2 mmol), potassium superoxide (0.288 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (50 mL) was stirred at room temperature for 30 h. The reaction mixture was treated with water (50 mL) to destroy any unchanged potassium superoxide and extracted several times with aqueous sodium chloride. The aqueous layer was acidified with dilute hydrochloric acid and extracted with benzene to give 60 mg (25%) of benzoic acid (17), mp 120-121 °C (mixture melting point). Removal of the solvent from the benzene-

extract gave a solid, which was chromatographed over silica gel. Elution with petroleum ether gave 27 mg (4%) of tetraphenylfuran (6a), mp 173-174 °C (mixture melting point), after recrystallization from ethanol. Further elution with a mixture (1:1) of benzene and petroleum ether gave 180 mg (23%) of 3,4,5,6-tetraphenylpyran-2-one (15), mp 166-167 °C (mixture melting point),²² after recrystallization from a mixture (1:1) of benzene and petroleum ether. Subsequent elution with benzene gave 300 mg (46%) of 2-hydroxy-2,4,5-triphenyl-3(2H)-furarone (18), mp 198-199 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IV.6.9 Attempted Reaction of Tetraphenylfuran (6a) with Potassium Superoxide. A mixture of 6a (0.93 g, 2.5 mmol), potassium superoxide (0.350 g, 5 mmol) and 18-crown-6 (0.622 g, 2.5 mmol) was stirred in benzene (60 mL) for 24 h and worked up as in the earlier case to give 760 mg (82%) of the unchanged starting material (6a), mp 173-174 °C (mixture melting point), after recrystallization from ethanol.

IV.6.10 Attempted Reaction of 2,5-Diphenylfuran (6b) with Potassium Superoxide. A mixture of 6b (0.44 g, 2 mmol), potassium superoxide (0.288 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (50 mL) was stirred at room temperature for

24 h and worked up as in the earlier cases to give 400 mg (90%) of the unchanged starting material (6b), mp 89-90 °C (mixture melting point).

IV.6.11 Attempted Reaction of 2,3,5-Triphenylfuran (6c) with Potassium Superoxide. A mixture of 6c (0.9 g, 3 mmol), potassium superoxide (0.2 g, 3 mmol) and 18-crown-6 (1.6 g, 6 mmol) in benzene (50 mL) was stirred at room temperature for 24 h and worked up as in the earlier cases to give 810 mg (90%) of the unchanged starting material (6c), mp 95-96 °C (mixture melting point).

IV.6.12 Reaction of 2,3-Diphenyl-1-indenone (31) with Potassium Superoxide. A mixture of 31 (1.12 g, 4 mmol), potassium superoxide (0.576 g, 8 mmol) and 18-crown-6 (0.530 g, 2 mmol) in benzene (50 mL) was stirred at room temperature for 10 h and worked up as in the earlier cases by treatment with water and extraction with aqueous sodium chloride. Acidification of the aqueous layer with dilute hydrochloric acid and extraction with benzene gave 230 mg (46%) of benzoic acid (17), mp 120-121 °C (mixture melting point). Removal of the solvent from the organic layer gave a solid, which was chromatographed over silica gel. Elution with petroleum ether gave 25 mg (2%) of 2,3-diphenylbenzofuran (47), mp 120-121 °C (mixture melting point), after recrystallization from ethanol. Further elution

with a mixture (1:9) of benzene and petroleum ether gave 370 mg (33%) of the unchanged starting material (31), mp 151-152 °C (mixture melting point). Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 75 mg (7%) of dibenzo[a,c]-13-fluorenone (44), mp 186-187 °C (mixture melting point),²⁰ after recrystallization from a mixture (1:4) of benzene and petroleum ether. Continued elution with a mixture (1:1) of benzene and petroleum ether gave 40 mg (3%) of 2,3-diphenyl-2-hydroxy-1-indanone (48), mp 128-129 °C, after recrystallization from a mixture (1:2) of benzene and petroleum ether.

IV.6.13 Attempted Reaction of 2,3-Diphenylbenzofuran (47) with Potassium Superoxide. Stirring a mixture of 47 (0.56 g, 2 mmol), potassium superoxide (0.288 g, 4 mmol) and 18-crown-6 (0.53 g, 2 mmol) in benzene (50 mL) for 24 h and workup in the usual manner gave 460 mg (82%) of the unchanged starting material (47), mp 120-121 °C (mixture melting point).

IV.6.14 Cyclic Voltammetry. Cyclic voltammetric experiments were carried out using Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat, a PAR Model 175 Universal Programmer, and a Kipp and Zonen X-Y recorder. Experiments were performed in a standard three compartment cell equipped

with a Pt-disc working electrode, Pt-wire counter electrode, and a saturated sodium chloride-calomel electrode (SSCE). Cyclic voltammograms were recorded in acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The direction of the initial scan was cathodic and the scan rate was 100 mV/s.

IV.6.15 Pulse Radiolysis. The pulse radiolysis experiments were carried out on a computer controlled pulse radiolysis apparatus.²³ The solutions of the substrates (0.2-0.5 mM) were taken in graduated 250 mL cylindrical reservoirs and deaerated by bubbling nitrogen for at least 30 min prior to irradiation. Nitrogen bubbling was continued in the reservoir from which the solution was allowed to flow gradually and continuously through a quartz cell (1 cm pathlength) that was irradiated with electron pulses in a right angle geometry with respect to the analyzing light. The irradiation was carried out with 5 ns electron pulses from the Notre Dame 8 MeV ARCO LP-7 linear accelerator using dose rates of $\sim 2 \times 10^{16}$ eV/g per pulse. Rate constants for the reaction with solvated electrons (e^-_{sol}) were determined from the kinetic analysis of the increased rate of decay of e^-_{sol} in presence of the substrate or rate of appearance of the radical anion.

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VITAE

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